Pergamon

Tetrahedron, Vol. 52, No. 4, pp. 1267-1278, 1996
Printed in Great Britain.
0040-4020/96 $15.00 + 0.00

0040-4020(95)00957-4

[2+2] Photocycloaddition of Homochiral 2(5*H*)-Furanones to Alkenes. First Step for an Efficient and Diastereoselective Synthesis of (+)- and (-)-Grandisol

Ramón Alibés, José L. Bourdelande, Josep Font*, Anna Gregori and Teodoro Parella

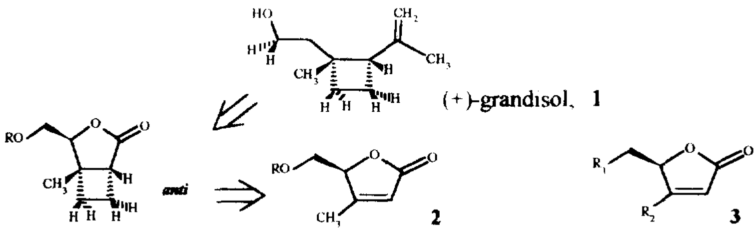
Unitat de Química Orgànica, Departament de Química, Universitat Autònoma de Barcelona, Bellaterra, 08193 Barcelona, Spain.

Abstract The [2+2] photocycloaddition of homochiral 5-alkyl-2(5*H*)-furanones to alkenes is studied in order to evaluate the influence of the stereogenic centre to induce facial diastereoselectivity. The major cycloadduct could be transformed, eventually, in (+)-grandisol. The existence of a charge-transfer complex between the furanone and electron rich substituted alkenes as well as the formation of a predominant conformation in 5-oxyalkylfuranones due to n-π interactions are discussed.

INTRODUCTION

The use of the [2+2] photocycloaddition of enones and α,β-unsaturated lactones to alkenes is a classic reaction in organic chemistry.[1,2] Cyclobutane rings, present in a variety of natural products, can be easily prepared following this procedure. In these cases, good facial diastereoselectivity is needed by the two moieties, although generally the reaction is carried out with symmetric olefins and the diastereoselection is then controlled by the substituents present in the α,β-unsaturated carbonylic compound. Steric and stereoelectronic effects have been invoked to govern the approach of the olefin to the enone creating the diastereofacial differentiation. Moreover, if this reagent contains a defined chiral centre, enantiomerically pure cycloadducts can be achieved.[3]

(+)-Grandisol, (+)-**1**, is the most important component in the sexual attracting pheromone of some insects, specially the cotton boll weevil, *Anthonomous grandis* Boheman.[4] It carries a cyclobutane ring and its total synthesis still atracts much attention ought to academic reasons and to the need for an economically viable preparation for the control of this pest insect in agriculture.[5] We have recognized part of the carbon skeleton of (+)- and (-)-grandisol in both cycloadducts formed when (*S*)-5-acyloxymethyl-4-methyl-2(5*H*)-furanones, **2**, reacts with ethylene under irradiation (scheme 1).



3a R$_1$: H; R$_2$: H
3b R$_1$: OH; R$_2$: H
3c R$_1$: OCOCF$_3$; R$_2$: H
3d R$_1$: OCOC(CH$_3$)$_3$; R$_2$: H
3e R$_1$: OCOC(CH$_3$)$_3$; R$_2$: CH$_3$
3f R$_1$: OCOCH$_3$; R$_2$: H
3g R$_1$: OCOCH$_3$; R$_2$: CH$_3$
3h R$_1$: OCH$_2$Ph; R$_2$: H

Scheme 1: Retrosynthetic analysis from (+)-grandisol to furanones

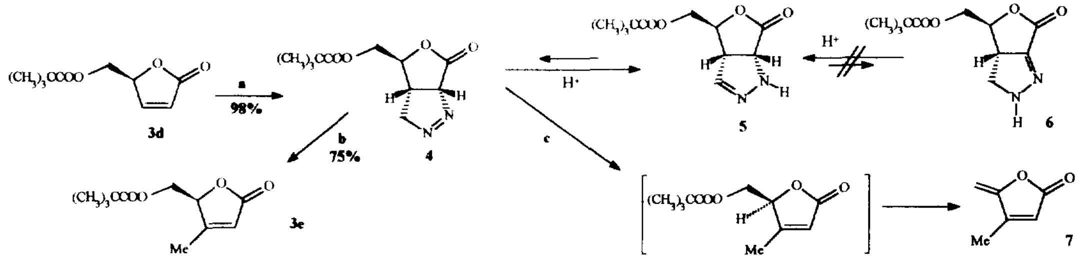
Since only the *anti* cycloadduct relates to (+)-grandisol, we thought that conveniently substituted lactones and alkenes could create an excess of this *anti* cycloadduct. Therefore we decided to study in detail the photocycloaddition of lactones **3a-h** to ethylene, extending the scope to other olefins mainly tetramethylethylene (TME) and vinylene carbonate. The substituent in the lactone should induce facial diastereoselectivity and being homochiral should lead to enantiomerically pure diastereomers with late immolation of the initial stereogenic centre in the synthetic plan.

The syntheses and the photochemical behaviour of some of these lactones have been already described.[3f,6] We wish to report here the revised and improved syntheses of some of these lactones as well as an overall picture of their photochemical behaviour that should help us to select those substituents with greater diastereofacial selectivity. Total syntheses of (+) and (-)-grandisol is reported in the following paper.

SYNTHESIS OF LACTONES

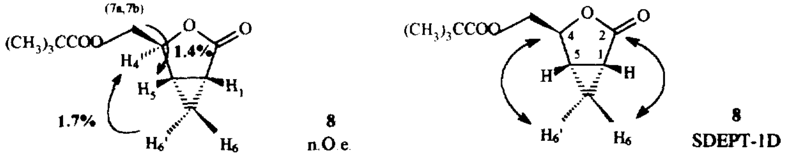
Lactone **3a** has been prepared from D-ribonolactone.[6] Lactone **3b** is commercial. Lactones **3c**, **3d**, **3f** and **3h** have been obtained from **3b** as already described.[3f,6] We describe herein the improved alternative synthesis of **3e** and the synthesis of the new **3g**.

The synthesis of (-)-(*S*)-4-methyl-5-pivaloyloxymethyl-2(5*H*)-furanone, **3e**, has been already described by Koga *et al.* from glutamic acid in 14% yield[3d] in 8 steps. We have followed an alternative route (scheme 2) where **3e** is obtained from **3d** in two steps in 74% yield. Addition of CH_2N_2 to **3d** affords a white solid identified as (3a*S*,4*S*,6a*R*)-4-pivaloyloxymethyl-3a,4,6,6a-tetrahydro-3*H*-furo[3,4-c]pyrazol-6-one, **4**. The ^{1}H-NMR spectrum of the reaction crude does not show the presence of any other diastereomer, thus indicating a high face diastereoselectivity during the CH_2N_2 1,3-dipolar cycloaddition. The configuration of the new chiral centres was determined by n.O.e. experiments.



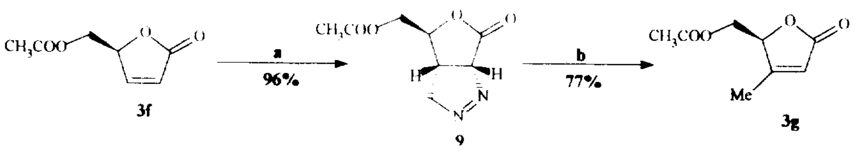
Reagents: a) CH_2N_2; b) dioxane, reflux; c) $CaCO_3$, toluene, reflux.
Scheme 2: Synthesis of (*S*)-4-methyl-5-pivaloyloxymethyl-2(5*H*)-furanone **3e**

The tautomerization of **4** to **5** but not to **6** (according to IR and DEPT spectra) is observed when acid traces are added to the solvent; this tautomerization is not rare in the cycloadditions of diazocompounds to alkenes,[7] although it has not been reported for compounds similar to **4**.[8] Pyrolysis of **4** in refluxing toluene in the presence of $CaCO_3$[8c] affords the unexpected 4-methyl-5-methylen-2(5*H*)-furanone **7** by elimination of pivalic acid. To avoid the influence of the carbonate we have treated **4** in refluxing dioxane without base, leading to **3e** as a solid in 75% yield.



Scheme 3

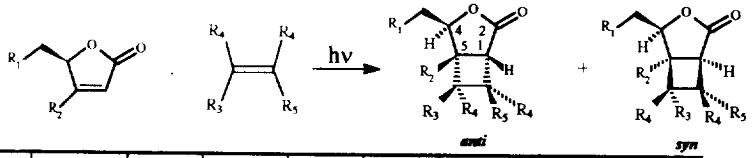
In this reaction a byproduct, **8** (1*R*,4*S*,5*S*)-4-pivaloyloxymethyl-3-oxabicyclo[3.1.0]hexan-2-one, is obtained as a white solid in a 5% yield. The cyclopropane *anti* structure of **8** has been assigned unequivocally from n.O.e. and SDEPT-1D[9] spectra (scheme 3). (-)-(*S*)-5-Acetyloxymethyl-4-methyl-2(5*H*)-furanone, **3g**, has easily been prepared from **3f** after addition of CH_2N_2 and pyrolysis of the pyrazoline **9** in 74% yield:



Reagents: a) CH_2N_2; b) dioxane, reflux.

PHOTOCYCLOADDITIONS

$R_3 = R_4 = R_5$: H ethylene
$R_3 = R_4 = R_5$: CH_3 TME
$R_3 - R_5$: OCOO, R_4 : H vinylene carbonate



lactone	R_1	R_2	alkene	T	solvent	filter	(%) anti	(%) syn	anti:syn	(%) other products
3a	H	H	TME	298	ether	quartz	(41)**10**	(14) **11**	74:26	--
3b	OH	"	"	"	"	"	(27)**12**	(10)**13**	73:27	--
"	"	"	"	253	"	"	(31)**12**	(11)**13**	74:26	--
3c	CF_3COO	"	"	"	"	"	(52)**14**	(12)**15**	80:20	--
3f	CH_3COO	"	"	"	"	"	(43)**20**	(11)**21**	79:21	--
3d	$(CH_3)_3CCOO$	"	"	298	"	"	(49)**16**	(11)**17**	82:18	--
"	"	"	"	"	acetone	pyrex	(15)**16**	(3)**17**	83:17	--
3h	$PhCH_2O$	"	"	"	ether	quartz	--	--	--:--	(52) **39**
3e	$(CH_3)_3CCOO$	CH_3	"	"	"	"	(22)**18**	(6)**19**	79:21	(17) **38**
"	"	"	"	"	"	"	(10)**18**	(3)**19**	77:23[a)]	(8) **38**
"	"	"	"	253	"	"	(29)**18**	(8)**19**	78:22	(25) **38**
"	"	"	"	298	acetone	pyrex	(5)**18**	(1)**19**	83:17	(3) **38**
3f	CH_3COO	H	ethylene	"	"	"	(60)**26**	(22)**27**	74:26	--
"	"	"	"	"	ether	quartz	--	--	--:--	--
3g	CH_3COO	CH_3	"	228	acetone	pyrex	(35)**28**	(30)**29**	56:46	--
3d	$(CH_3)_3CCOO$	H	"	"	"	"	(46)**22**	(13)**23**	78:22	--
"	"	"	"	253	"	"	(45)**22**	(14)**23**	76:24[b)]	--
"	"	"	"	"	"	"	(38)**22**	(10)**23**	79:21[c)]	--
"	"	"	"	298	ether	quartz	--	--	--:--	--
"	"	"	"	253	"	"	--	--	--:--	--
3h	$PhCH_2O$	"	"	195	acetone	pyrex	--	--	--:--	(44) **39**
3e	$(CH_3)_3CCOO$	CH_3	"	"	"	"	(62)**24**	(38)**25**	62:38	--
"	"	"	"	228	"	"	(43)**24**	(27)**25**	62:38	--
"	"	"	"	258	"	"	(37)**24**	(23)**25**	62:38	--
"	"	"	"	228	"	quartz	(6)**24**	(4)**25**	60:40	--
3d	$(CH_3)_3CCOO$	H	vinylene carbonate	195	"	pyrex	(43)**30**	(7)**31**	86:14	--
"	"	"	"	"	ether	quartz	(<1)**30**	(<1)**31**	--:--	--
3h	$PhCH_2O$	"	"	"	acetone	pyrex	--	--	--:--	(54) **39**
3e	$(CH_3)_3CCOO$	CH_3	"	"	"	"	(48)**32**	(6)**33**	88:12	--
"	"	"	"	"	ether	quartz	(<1)**32**	(<1)**33**	--:--	--
3h	$PhCH_2O$	H	"	"	acetone	pyrex	--	--	--:--	(49) **39**

Table 1: Photocycloadducts yields under different conditions. a) λ = 254 nm; b) irradiation time: 1h; c) irradiation time: 2h.

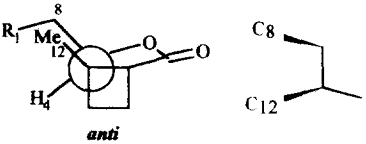
All lactones, with the only exception of **3h** (Table 1), afforded two cycloadducts under irradiation with a medium pressure Hg lamp in the presence of ethylene, TME or vinylene carbonate. Both cycloadducts were separated by column chromatography and their relative configurations were determined by NMR as follows:

a) Cycloadducts of lactones, $R_2 = H$.

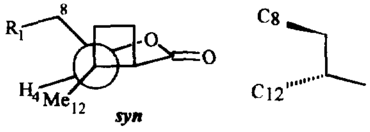
Since cycloadducts are rigid, the coupling constants between H_4 and H_5, $J_{4,5}$, have been used to elucidate the structure: *anti* isomers must show small $J_{4,5}$ (larger dihedral angle) while *syn* isomers must have large $J_{4,5}$ (smaller dihedral angle). In all cases the major cycloadduct showed the $J_{4,5}$ coupling constant ranging between 1.2 and 2.0 values while in the minor cycloadduct $J_{4,5}$ was 5.0-6.0 Hz (see experimental section).

b) Cycloadducts of lactones, $R_2 = CH_3$.

Since hydrogen in the position 5 has been substituted for a CH_3 group we have used the chemical shift of this group to assign the cycloadducts. The "steric compression" in the *anti* adduct is much larger than in the *syn* one; as a consequence, the resonance of the C-12 carbon atom, i.e. the methyl group, in the *anti* diastereomer has to appear at higher fields.[10] As described in the experimental section the major cycloadducts (*anti*) present the smallest chemical shift for C-12 (δ=16.4-17.8) while the minor adducts present larger δ (δ=21.1-21.3).



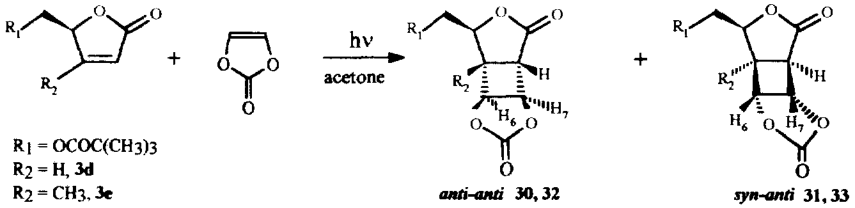
anti



syn

c) Vinylene carbonate as alkene.

When the alkene is vinylene carbonate, four new stereogenic centers are created. Only the *anti-anti* and the *syn-anti* isomers where detected by g.l.c. and isolated. Assignment of the ¹H-NMR signals were done from COSY spectra. In all cycloadducts, the coupling constants between H_1 and H_7, $J_{1,7}$, were small (1.22 for **30**) or smaller than the analytical error (**31, 32, 33**) (see experimental section). Also, $J_{5,6}$, (when R_2=H) were small (2.44-2.93). These data are consistent with an *anti* relative configuration of H_1-H_7 and H_5-H_6 pairs only present in the *anti-anti* and *syn-anti* isomers.



R_1 = OCOC(CH3)3
R_2 = H, **3d**
R_2 = CH3, **3e**

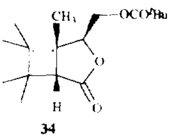
***anti-anti* 30, 32**

***syn-anti* 31, 33**

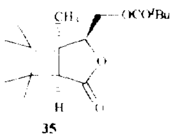
MECHANISM AND DIASTEREOSELECTIVITY

We have investigated the effect in the *anti-syn* cycloadduct ratio due to R_1, R_2, R_3, R_4, R_5, the temperature, the solvent and the filter. The Table 1 compiles the results of these experiments. On the other hand, the generally accepted mechanism for the photocycloaddition of enones to alkenes[1b,11,12] suggests that the triplet state of the enone and some biradicals are involved along the reaction pathway. In our case these radicals could be **34-37**. 1,4-Biradicals like **34** and **35** with a first new C-C bond at the α-position have been proposed as the more stable among the four possible (**34-37**) in the [2+2]-photocycloaddition of ethylene and 5-

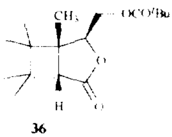
alkoxy-2(5*H*)-furanones, which are similar to our substrates[3d] The ocurrence of such radicals could be the reason for the formation of compound **38** through diradical **34**. An ene reaction can be discarded since the ratio **38:cycloadducts** is not dependent on the temperature (table 1).[13] The configuration of C-3 in **38** has been determined by differential n.O.e:



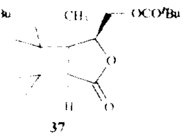
34



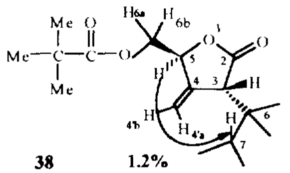
35



36

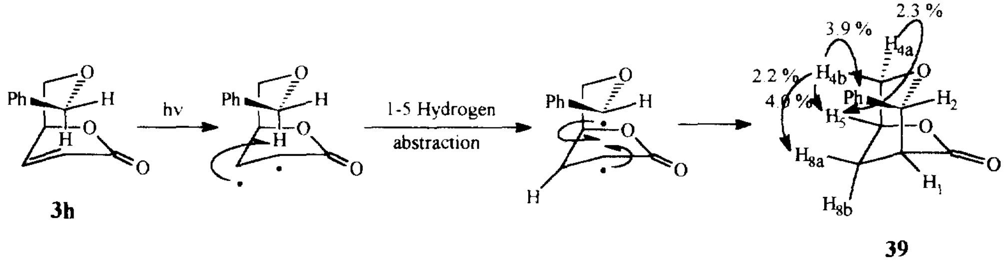


37



38

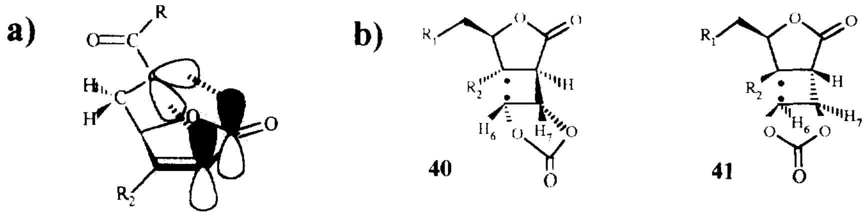
The evolution of the photocycloaddition reaction through radicals can explain the unexpected formation of compound **39** (see scheme 4). This bicyclic lactone is obtained as the only product when we tried the photocycloaddition of **3h** and any olefine; yields of **39** ranged 44-54% (table) depending on the alkene, the solvent, the filter and the irradiation time. It is worth to remark that we have isolated **39** with only one configuration in C-2 showing no epimerization. All peaks assignments in the ^1H and ^{13}C-NMR spectra and the configurational analysis of the new chiral carbons have been done from COSY and n.O.e. spectra (scheme 4). The photochemical formation of **39** under direct and sensitized irradiation as a unique diastereomer suggests a very fast reaction and a very rigid geometry:



Scheme 4

As shown in the table 1 there is a great influence of the solvent. An electron rich olefine as TME reacts with good yield in ether under direct irradiation but not in acetone with a pyrex filter. On the contrary, electron poor olefines react efficiently in acetone/pyrex but not in ether/quartz. These results are parallel to those described for the addition under direct irradiation of cyclopentenone to different alkenes.[12] Schuster *et al.* proved that any alkene deactivates efficiently the excited triplet state of the enone but only the 1,4-biradicals formed with electron rich alkenes perform efficient ring closure while the 1,4-biradicals formed with electron poor alkenes decompose or return to the ground state of the enone plus olefine in a way faster than forming the cycloadducts. It is known, also that the π-π^* triplet of the 2(5*H*)-furanones can be generated by sensitization with acetone[2b] and that the photodecomposition of the cycloadducts or their precursors can be avoided by filtering with pyrex (acetone is still excited at λ>290nm). That allows to understand why electron poor olefines react in acetone/pyrex but not in ether/quartz: the acetone guarantees the formation of the reactive triplet of the enone and the pyrex filter avoids the photodegradation. However, no satisfactory explanation exists to our finding that TME does not react in acetone/pyrex: if the triplet of the 2(5*H*)-furanone is formed and the 1,4-biradical intermediates or the cycloadducts do not decompose under direct irradiation in ether/quartz they should react in the "mild" conditions of acetone/pyrex. We have proposed[14] the formation of a charge-transfer complex, with an *anti* approach, between the ground state of the 2(5*H*)-furanone and the TME. Now, both faces of the furanone would be "blocked" and the approach of the excited acetone as well as the subsequent energy transfer would be prevented. This could explain the absence of reaction in acetone/pyrex but the furanone would still be able to absorb light in ether/quartz to generate the reactive triplet and the formation of cycloadducts.

When photocycloaddition is efficient the dominant adduct is always *anti*. The bulkiest the R_1 substituent in C-5, the greatest the *anti:syn* ratio for any olefine. This confirms the existence of the stereoselection exercised by the stereogenic center of the furanone. When R_2=H, we have already suggested the existence of stereoelectronic effects by the formation of a predominant conformation with an n-π interaction between the non-bonding electrons of oxygen with the π orbital of the butenolide[3f] (scheme 5a) in furanones where R_1 is -OCO-R. This conformation would force the olefine to approach the furanone by the α face favouring the *anti* adduct. The existence of this conformation does not depend on the nature of R in CH_2-OCOR and the diastereomeric excess for R=CH_3 is similar to the diastereomeric excess for R=$(CH_3)_3C$.



Scheme 5

The extension of the effect of R_2 on the *anti:syn* ratio depends on the alkene: for ethylene the ratio decreases from 78:22 (R_2=H) to 62:38 (R_2=CH_3); for TME it passes from 82:18 to 79:21; but for vinylene carbonate it increases from 86:14 (R_2=H) to 88:12 (R_2=CH_3). Results for ethylene and TME are parallel to those described by Scharf *et al.* for the photosensitized [2+2]-cycloaddition of ethylene to 5-alkoxy-2(*5H*)-furanones.[3g] They found that the *anti:syn* ratio decreased when the H in position 4 was replaced for Me, Et, or iPr, and they explained this change on the basis of the pyramidalization of the β-carbon and the homoanomeric effect in the 1,4-biradical of the $(^3\pi\text{-}\pi)^*$-furanones. In our system only the pyramidalization effect can be operative and it does not explain the reversion found for vinylene carbonate. Probably for this olefine the many steric effects appearing in the last step of the cycloaddition play a relevant influence in the rate of such a process towards the *anti* or the *syn* adducts. The carbonate moiety in the diradical **40** is a rigid cycle that cannot relax properly the steric hindrance exercised by the bulky R_1 in this last step. As this interaction does not appear in the ring closure of **41**, this intermediate could be preferred, thus affording the *anti* cycloadduct as the major one (see scheme 5b). The effect of the temperature is small in the *anti:syn* ratio but large in the cycloadduct yields: they increase at lower temperatures.

Finally it is worth to mention that the more efficient ways to generate an *anti* cycloadduct that could be transformed in (+)-grandisol are the low temperature photocycloaddition of furanone **3e** to ethylene in acetone/pyrex (70%, 62:38) and the addition of the same furanone to vinylene carbonate at the same conditions (54%, 88:12).

ACKNOWLEDGEMENTS

Financial support from DGICYT (Spain) project PB 92-0605 and CIRIT (Generalitat de Catalunya) are gratefully acknowledged. We also thank Servei de Ressonància Magnètica Nuclear (UAB) for allocating instrumental time to this project.

EXPERIMENTAL SECTION

Melting points were determined on a Kofler hot stage and are uncorrected. Optical rotations were obtained on a Propol polarimeter, Model Dr. Kerchen. Distillations were effected on a rotational distillator, Büchi Model KRV 65/30 (only external or oven temperature are given).

The 250 MHz ^{1}H-NMR and the 62.5 MHz ^{13}C-NMR spectra were recorded on a Bruker spectrometer Model AC250 and the 400 MHz ^{1}H-NMR and 100 MHz ^{13}C-NMR spectra were recorded on a Bruker spectrometer Model AM400WB. Uv and IR spectra were recorded on a Hewlett-Packard 8452A and a Nicolet 20X spectrophotometers respectively.

Gas chromatographic analyses were performed on a Hewlett-Packard model 5930 instrument with a capillary column Hewlett-Packard Ultra 1 (crosslinked methyl silicone gum, 12m x 0.2mm x 0.3 µm). Ms spectra were recorded with a Hewlett-Packard apparatus Model 5989. Microanalyses were performed either at the Instituto de Química Bio-Orgánica C.S.I.C., Barcelona or at the Servei d'Anàlisi Elemental of the Universitat Autònoma de Barcelona.

(3a*S*,4*S*,6a*R*)-4-Pivaloyloxymethyl-3a,4,6,6a-tetrahydro-3*H*-furo[3,4-*c*]pyrazol-6-one, 4

To a stirred solution of **3d** (534 mg, 2.74 mmol) in THF (4 mL) at -5 °C an ethereal solution of diazomethane (*ca.* 7.61 mmol), prepared from *N*-methyl-*N*-nitroso-4-toluenesulfonamide (2.18 g, 10.17 mmol), was added. The mixture was stirred at room temperature for 48 h protected from light. After cooling, the solvents were evaporated to afford **4** (645 mg, 98% yield) as colorless needles; mp: 127-129 °C (ether-pentane); $[\alpha]_D^{27}$: -321.4° (*c* 0.84, CH_3COCH_3), ^{1}H-NMR (400 MHz, d^6-acetone) δ 1.20 (s, 9H, $(CH_3)_3C$), 3.1 (dddd, $J_{3a,6a}$: 9.4 Hz, $J_{3a,3'}$: 7.6 Hz, $J_{3a,3}$: 4.6 Hz, $J_{3a,4}$: 4.0 Hz, 1H, H-3a), 4.27 (dd, J_{gem}: 12.2 Hz, $J_{7a,4}$: 4.2 Hz, 1H, H-7a), 4.35 (dd, J_{gem}: 12.2 Hz, $J_{7b,4}$: 3.0 Hz, 1H, H-7b), 4.52 (ddd, $J_{4,7a}$: 4.2 Hz, $J_{4,7b}$: 3.0 Hz, $J_{4,3a}$: 4.0 Hz, 1H, H-4), 4.95 (ddd, J_{gem}: 18.8 Hz, $J_{3',3a}$: 7.6 Hz, $J_{3',6a}$: 1.9 Hz, 1H, H-3'), 5.02 (ddd, J_{gem}: 18.8 Hz, $J_{3,3a}$: 4.6 Hz, $J_{3,6a}$: 2.4 Hz, 1H, H-3), 5.75 (ddd, $J_{6a,3a}$: 9.4 Hz, $J_{6a,3}$: 2.4 Hz, $J_{6a,3'}$: 1.9 Hz, H-6a); ^{13}C-NMR (20 MHz, d^6-acetone) δ 27.4 (C-10), 34.8 (C-3a), 39.3 (C-9), 65.8 (C-3), 83.53 (C-7), 86.7 (C-6a), 94.9 (C-4), 169.1 (C-8), 177.8 (C-6); IR (KBr) ν 2979, 2946, 2879, 1778 ($\nu_{C=O}$), 1733 ($\nu_{C=O}$), 1483, 1368, 1349, 1266, 1191 (ν_{C-O}), 1151, 1069, 943 cm^{-1}; Ms m/z (%) ($C_{11}O_4H_{16}N_2$) 241 (M^++1, 0.2), 212 (M^+-N_2, 0.1), 168 (212-CO_2, 0.1), 155 (212-$(CH_3)_3C$, 0.1), 140 (155-CH_3, 1-H), 128 (2.4), 111 (212-$(CH_3)_3CCO_2$, 8.4), 97 (111-CH_2, 14.0), 85 (10.3), 68 (17.6), 57 ($(CH_3)_3C$, 100), 41 (33.5).

(3a*S*,4*S*,6a*R*)-4-Pivaloyloxymethyl-3a,4,6,6a-tetrahydro-1*H*-furo[3,4-*d*]-pyrazol-6-one, 5

^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.25 (s, 9H, $(C\underline{H}_3)_3C$), 3.80 (ddd, $J_{3a,6a}$: 9.9 Hz, $J_{3a,4}$: 1.0 Hz, $J_{3a,3}$: 1.0 Hz, 1H, H-3a), 4.20 (dd, J_{gem}: 12.4 Hz, $J_{4a,4}$: 2.6 Hz, 1H, H-4a), 4.4 (dd, J_{gem}: 12.4 Hz, $J_{4b,4}$: 2.6 Hz, 1H, H-4b), 4.42 (d, $J_{6a,3a}$: 9.9 Hz, 1H, H-6a), 4.80 (ddd, $J_{4,4a}$: 2.6 Hz, $J_{4,4b}$: 2.6 Hz, $J_{4,3a}$: 1.0 Hz, 1H, H-4), 6.80 (d, $J_{3,3a}$: 1.2 Hz, 1H, H-3); ^{13}C-NMR (20 MHz, $CDCl_3$) δ 26.9 (CH_3, C-10), 38.6 (C, C-9), 50.6 (CH, C-3a), 59.1 (CH, C-6a), 64.8 (CH_2, C-7), 78.8 (CH, C-4), 141.4 (CH, C-3), 175 (C=O, C-8), 177 (C=O, C-6); IR (film) ν 3327 (ν_{N-H}), 3032, 2975, 2941, 2914, 2875, 1778 ($\nu_{C=O}$), 1731 ($\nu_{C=O}$), 1480, 1460, 1398, 1367, 1341, 1282, 1148, 1071, 1036, 925, 856 cm^{-1}; Ms m/z (%) ($C_{11}O_4H_{16}N_2$) 241 (M^++1, 0.2), 212 (M^+-N_2, 0.1), 168 (212-CO_2, 0.1), 155 (212-$(CH_3)_3C$, 0.1), 140 (155-CH_3, H-1), 128 (2.4), 111 (212-$(CH_3)_3CCO_2$, 8.4), 97 (111-CH_2, 14.0), 85 (10.3), 68 (17.6), 57 (100), 41 (33.5).

4-methyl-5-methylen-2(5*H*)-furanone, 7

A mixture of **4** (542 mg, 2.26 mmol) and $CaCO_3$ (1.0 g) in 31 mL of toluene was heated at reflux for 20 h. The mixture was cooled and the precipitate filtered off. The solvent was evaporated and the residue chromatographed on silica gel (mixtures of ethyl acetate/hexanes as eluents) to afford **7** (186 mg, 75% yield) as an oil; ^{1}H-NMR (80 MHz, $CDCl_3$) δ 2.16 (d, $J_{4',3}$: 1.4 Hz, 3H, CH_3-4'), 4.88 (dd, J_{gem}: 2.8 Hz, $J_{6,3}$: 0.8 Hz, 1H, H-6), 5.14 (dd, J_{gem}: 2.8 Hz, $J_{6',3}$: 1.8 Hz, 1H, H-6'), 5.96 (ddq, $J_{3,6'}$: 1.8 Hz, $J_{3,4}$: 1.4 Hz, $J_{3,6}$: 0.8 Hz, 1H, H-3); ^{13}C-NMR (20 MHz, $CDCl_3$) δ 11.8 (C-4'), 94.2 (C-6), 118.0 (C-3), 154.5 (C-4), 156.5 (C-5), 169.0 (C-2); IR (film) ν 3113, 2957, 2927, 2856, 1766 ($\nu_{C=O}$), 1653 ($\nu_{C=C}$), 1613 ($\nu_{C=C}$), 1439, 1333, 1259, 1232, 1173 (ν_{C-O}), 1123, 1079, 971, 892 cm^{-1}; Ms m/z (%) ($C_6H_6O_2$) 111 (M^++1, 23), 110 (M^+, 100), 82 (31), 68 (56.9), 67 (M^++1-CO_2, 12.2), 54 (14.7), 53 (68-CH_3, 15.6), 50 (15), 42 (49.6), 41 (10.2).

(-)-(*S*)-4-Methyl-5-pivaloyloxymethyl-2(5*H*)-furanone, 3e

A solution of **4** (645 mg, 2.69 mmol) in 40 mL of dioxane was heated at reflux for 51 h. The solvent was evaporated and the residue chromatographed on silica gel using an ethyl acetate/hexane 1:3 mixture to afford **3e** (428 mg, 75% yield) as colorless needles; mp: 67-69 °C (ethyl acetate-hexane); $[\alpha]_D^{20}$: -74.31 ° (*c* 2.09, $CHCl_3$); ^{1}H-NMR (80 MHz, $CDCl_3$) δ 1.18 (s, 9H, $(C\underline{H}_3)_3C$), 2.12 (m, 3H, $C\underline{H}_3$-4'), 4.36 (dd, J_{gem}: 12.2 Hz,

$J_{6a,5}$: 4.9 Hz, 1H, H-6a), 4.43 (dd, J_{gem}: 12.2 Hz, $J_{6b,5}$: 2.5 Hz, 1H, H-6b), 5.01 (br, 1H, H-5), 5.82-5.96 (m, 1H, H-3); ^{13}C-NMR (20 MHz, $CDCl_3$) δ 13.6 (C-4'), 26.9 (C-9), 38.7 (C-8), 61.2 (C-6), 82.1 (C-5), 118.4 (C-3), 165.0 (C-4), 172.1 (C-7), 177.6 (C-2); IR (KBr) ν 3132, 2975, 2877, 1762 ($\nu_{C=O}$), 1726 ($\nu_{C=O}$), 1646 ($\nu_{C=C}$), 1482, 1443, 1397, 1367, 1286, 1165, 1095, 1048, 946 cm^{-1}; Ms m/z (%) ($C_{11}O_4H_{16}$) 213 (M^++1, 5.4), 182 (1.3), 156 (M^++1-C_4H_9, 0.7), 154 (2.3), 129 (1.1), 111 (M^+-$(CH_3)_3CCO_2$, 12.8), 98 (112-CH_2, 23.5), 97 (12.9), 85 (13.8), 69 (12.8), 57 ($(CH_3)_3C$,100),41 (97).

(1*R*,4*S*,5*S*)-4-Pivaloyloxymethyl-3-oxabicyclo[3.1.0]hexan-2-one, 8

mp: 69-71 °C (ethyl acetate-pentane); $[\alpha]_D^{25}$: -6.33 ° (*c* 1.10, $CHCl_3$); ^{1}H-NMR (250 MHz, $CDCl_3$) δ 0.88 (m, 1H, H-6), 1.18 (s, 9H, $(C\underline{H}_3)_3C$), 1.20 (m, 1H, H-6'), 2.08 (m, 2H, H-1 i H-5), 4.23 (dd, J_{gem}: 12.2 Hz, $J_{7a,4}$: 3.4 Hz, 1H, H-7a), 4.28 (dd, J_{gem}: 12.2 Hz, $J_{7b,4}$: 3.4 Hz, 1H, H-7b), 4.53 (dd, $J_{4,7a}$: 3.4 Hz, $J_{4,7b}$: 3.4 Hz, 1H, H-4); ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ 11.3 (CH_2, C-6), 17.3 (CH, C-5), 19.3 (CH, C-1), 26.8 (CH_3, $(\underline{C}H_3)_3C$), 38.6 (C, $\underline{C}(CH_3)_3$), 64.8 (CH_2, C-7), 77.6 (CH, C-4), 175.9 (C=O), 177.9 (C=O); IR (KBr) ν 3078, 2975, 2875, 1764, 1722 ($\nu_{C=O}$), 1482, 1345, 1280, 1190, 1175, 1146, 1120, 1036 cm $^{-1}$; Ms m/z (%) 212 (M^+, 2), 182 (2), 109 (47), 97 (100), 85 (34), 69 (21), 57 (78), 54 (10). Anal. Calc. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.65. Found: C, 62.24; H, 7.65.

(3a*S*,4*S*,6a*R*)-4-Acetyloxymethyl-3a,4,6,6a-tetrahydro-3*H*-furo[3,4-*c*]pyrazol-6-one, 9

To a stirred solution of **3f** (549 mg, 3.52 mmol) in THF (5 mL) at -5 °C an ethereal solution of diazomethane (*ca.* 7.61 mmol), prepared from *N*-methyl-*N*-nitroso-4-toluenesulfonamide (2.14 g, 9.98 mmol), was added. The mixture was stirred at room temperature for 48 h protected from light. After cooling, the solvents were evaporated to afford **9** (699 mg, 96% yield) as colorless needles; mp: 68-70 °C (ether-pentane); $[\alpha]_D^{27}$:-414.5 ° (*c* 0.82, CH_3COCH_3); ^{1}H-NMR (250 MHz, d^6-acetone) δ 2.05 (s, 3H, Me-CO), 3.03 (dddd, $J_{3a,6a}$: 9.51 Hz, $J_{3a,3'}$: 7.3 Hz, $J_{3a,3}$: 4.39 Hz, $J_{3a,4}$: 4.39 Hz, 1H, H-3a), 4.25 (dd, J_{gem}: 12.43 Hz, $J_{7a,4}$: 5.12 Hz, 1H, H-7a), 4.32 (dd, J_{gem}: 12.43 Hz, $J_{7b,4}$: 2.19 Hz, 1H, H-7b), 4.48 (ddd, $J_{4,7a}$: 5.12 Hz, $J_{4,3a}$: 4.39 Hz, $J_{4,7b}$: 2.19 Hz, 1H, H-4), 4.88 (ddd, J_{gem}: 18.28 Hz, $J_{3',3a}$: 7.3 Hz, $J_{3',6a}$: 2.2 Hz, 1H, H-3'), 4.98 (ddd, J_{gem}: 18.28 Hz, $J_{3,3a}$: 4.39 Hz, $J_{3,6a}$: 2.2 Hz, 1H, H-3), 5.7 (ddd, $J_{6a,3a}$: 9.51 Hz, $J_{6a,3}$: 2.2 Hz, $J_{6a,3'}$: 2.2 Hz, 1H, H-6a); ^{13}C-NMR (62.5 MHz, d^6-acetone) δ: 20.46 (CH_3, $\underline{C}H_3$-CO), 34.68 (CH, C-3a), 65.70 (CH, C-3), 83.4 (CH, C-6a), 86.3 (CH_2, C-7), 94.64 (CH, C-4), 169.28 (C-8), 170.60 (C-6); IR (film) ν 2996, 2959, 1777 ($\nu_{C=O}$), 1741 ($\nu_{C=O}$), 1433, 1378, 1339, 1226, 1184, 1104, 1078, 1043, 944 cm^{-1}; Ms m/z (%) 198 (M^+, 1), 156 (1), 128 (3), 111 (2), 110 (5), 98 (19), 97 (27), 69 (18), 68 (23), 53 (4), 43 (100). Anal. Calc. for ($C_8H_{10}N_2O_4$): C, 48.47; H, 5.09; N, 14.14. Found: C, 48.58; H, 5.26; N, 13.94.

(-)-(*S*)-4-Methyl-5-acetyloxymethyl-2(5*H*)-furanone, 3g

A solution of **9** (650 mg, 3.28 mmol) in 50 mL of dioxane was heated at reflux for 51 h. The solvent was evaporated and the residue chromatographed on silica gel using an ethyl acetate/hexane 1:3 mixture to afford **3g** (430 mg, 77% yield) as colorless needles; mp: 31-33 °C (ether-pentane); $[\alpha]_D^{25}$: -53.74 ° (*c* 1.13, $CHCl_3$); ^{1}H-NMR (250 MHz, $CDCl_3$) δ 2.0 (s, 3H, Me), 2.08 (s, 3H, Me), 4.20 (dd, J_{gem}: 12.42 Hz, $J_{6,5}$: 5.12 Hz, 1H, H-6), 4.42 (dd, J_{gem}: 12.42 Hz, $J_{6,5}$: 2.93 Hz, 1H, H-6), 4.97 (broad, 1H, H-5), 5.68 (broad, 1H, H-3); ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ 13.72 ($\underline{C}H_3$-C=), 20.37 ($\underline{C}H_3$-CO), 61.6 (C-6), 81.8 (C-5), 118.3 (C-3), 164.8 (C-4), 170.2 (C-7), 172.2 (C-2); IR (film) ν 3107, 2952, 1744 ($\nu_{C=O}$), 1643, 1384, 1227, 1175, 1153, 1049, 945 cm^{-1}; Ms m/z (%) 171 (M^++1, 1), 141 (3), 140 (33), 98 (69), 97 (9), 70 (5), 69 (9), 43 (100). Anal. Calc. for ($C_8H_{10}O_4$): C, 56.47; H, 5.92. Found: C, 56.53; H, 6.08.

General experimental procedure for photocycloadditions of 2(5*H*)-furanones with TME, vinyl ethylene and ethylene.

Irradiations were performed in a small conventional photochemical reactor (two-necked 50 mL raction vessel and a water-jacketed immersion well) using a medium pressure 125W mercury lamp (Philips HPK-125). Water was used for refrigeration of the immersion well jacket. The progress of the reaction was monitored by glc.

(1*S*,4*S*,5*R*)-5-methyl-4-pivaloyloxymethyl-6,6,7,7-tetramethyl-3-oxabicyclo[3.2.0]heptan-2-one, 18 (1*R*,4*S*,5*S*)-5-methyl-4-pivaloyloxymethyl-6,6,7,7-tetramethyl-3-oxabicyclo[3.2.0]heptan-2-one, 19 and (3*R*,5*S*)-4-methylen-3-(1,1,2-trimethylpropyl)-5-pivaloyloxymethyl-2-oxolanone, 38.

A solution of **3e** (181 mg, 0.86 mmol) and tetramethylethylene (TME) (1 mL, 8.42 mmol) in dry ether (45 mL) was irradiated at -20 °C for 7 h through quartz under Ar atmosphere. The solvent was removed at reduced pressure and the crude was chromatographed on silica gel (0→12% ether in hexane as eluent).

The first fraction gave **38** (39 mg, 17% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.88 (d, $J_{7a,7}$: 6.8 Hz, 3H, CH_3-7a), 0.87 (s, 3H, CH_3-6), 0.91 (d, $J_{7b,7}$: 6.8 Hz, 3H, CH_3-7b), 0.96 (s, 3H, CH_3-6), 1.17 (s, 9H, $(CH_3)_3C$-), 2.05 (heptet, $J_{7a,7}$: 6.8 Hz, $J_{7b,7}$: 6.8 Hz, 1H, H-7), 3.10 (m, 1H, H-3), 4.24 (dd, J_{gem}: 12.2 Hz, $J_{6a,5}$: 5.5 Hz, 1H, H-6a), 4.38 (dd, J_{gem}: 12.2 Hz, $J_{6b,5}$: 2.7 Hz, 1H, H-6b), 5.02 (m, 1H, H-5), 5.16 (dd, J_{gem}: 1.7 Hz, $J_{4'a,3}$: 1.7 Hz, 1H, H-4'a), 5.27 (dd, J_{gem}: 1.7 Hz, $J_{4'b,5}$: 1.7 Hz, 1H, H-4'b); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 17.2, 17.5, 20.2, 20.4, 27.1, 31.8, 38.8, 40.7, 52.0, 64.5, 79.8, 112.4, 141.9, 175.6, 178.2; IR (film) ν 2955, 2929, 2880, 2862, 1777 ($\nu_{C=O}$), 1736 ($\nu_{C=O}$), 1632 ($\nu_{C=C}$), 1452, 1380, 1272, 1152, 1080, 948 cm^{-1}; Ms m/z (%) ($C_{17}H_{28}O_4$) 297 (M^++1, 0.4), 212 (M^+-C_6H_{12}, 13.0), 195 (M^+-$(CH_3)_3CCO_2$, 0.4), 151 (195-CO_2, 1.2), 128 (23.9), 111 (195-C_6H_{12}, 14.4), 110 (64.3), 69 (84-CH_3, 11.2), 67 (111-CO_2, 6.7), 57 ($(CH_3)_3C$, 100), 43 (73), 41 (72); Ms (CI/NH_3) m/z (%) 314 (M^++18).

The second fraction gave **19** (14 mg, 6% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.02 (s, 6H, 2xCH_3), 1.19 (s, 3H, CH_3), 1.25 (s, 9H, $(CH_3)_3C$), 1.3 (s, 3H, CH_3), 1.4 (s, 3H, CH_3), 2.4 (s, 1H, H-1), 4.22 (dd, $J_{4,8a}$: 7.8 Hz, $J_{4,8b}$: 2.3 Hz, 1H, H-4), 4.35 (dd, J_{gem}: 12.5 Hz, $J_{4,8b}$: 2.3 Hz, 1H, H-8b), 4.47 (dd, J_{gem}: 12.5 Hz, $J_{4,8a}$: 7.8 Hz, H-8a); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.1, 21.2, 21.8, 24.9, 27.1 (C-11), 27.2 (C-12, C-6a, C-7a, C-7b), 38.8 (C-10), 39.8, 43.5, 46.5 (C-6, C-7, C-5), 53.1 (C-1), 62.9 (C-8), 88.4 (C-4), 178.0 (C-9), 178.8 (C-2); IR (film) ν 2983 , 2927, 2871, 1772 ($\nu_{C=O}$), 1731 ($\nu_{C=O}$), 1487, 1385, 1279, 1154, 1039, 923 cm^{-1}; Ms m/z (%) ($C_{17}H_{28}O_4$) 297 (M^++1, 1.8), 253 (M^++1-CO_2, 0.3), 213 (M^++1-C_6H_{12}, 0.3), 196 (4.2), 195 (M^+-$(CH_3)_3CCO_2$, 5.7), 181 (196-CH_3, 4.5), 167 (181-CH_2, 1.9), 149 (5.5), 111 (13.8), 97 (26.1), 85 (15.2), 84 (C_6H_{12}, 92.2), 83 (C_6H_{12}-1, 100), 69 (84-CH_3, 43.0), 57 ($(CH_3)_3C$, 68.4), 41 (36.8).

The third fraction gave **18** (55 mg, 22% yield); ^{1}H-NMR (80 MHz, $CDCl_3$) δ 1.0 (s, 6H, 2xCH_3), 1.19 (s, 9H, $(CH_3)_3C$), 1.2 (s, 3H, CH_3), 1.3 (s, 3H, CH_3), 1.35 (s, 3H), 2.4 (s, 1H, H-1), 4.0 (dd, J_{gem}: 11.7 Hz, $J_{8a,4}$: 2.5 Hz, 1H, H-8a), 4.35 (dd, J_{gem}: 11.7 Hz, $J_{8b,4}$: 2.5 Hz, 1H, H-8b), 4.62 (dd, $J_{4,8a}$: 2.5 Hz, $J_{8b,4}$: 2.5 Hz, 1H, H-4); ^{13}C-NMR (20 MHz, $CDCl_3$) δ: 16.4 (C-12), 21.2, 22.2, 27.1 (C-11), 27.5 (C-6a, C-6b, C-7a, C-7b), 38.7 (C-10), 40.3, 43.0, 44.3 (C-6, C-7, C-5), 53.4 (C-1), 63.8 (C-8), 80.0 (C-4), 177.4 (C-9), 177.8 (C-2); IR (film) ν 2955 , 2933, 2875, 1773 ($\nu_{C=O}$), 1735 ($\nu_{C=O}$), 1479, 1461, 1397, 1378, 1283, 1149, 1038, 946 cm^{-1}; Ms m/z (%) ($C_{17}H_{28}O_4$) 297 (M^++1, 0.8), 253 (M^++1-CO_2, 0.2), 213 (M^++1-C_6H_{12}, 0.3), 196 (M^++1-$(CH_3)_3CCO_2$, 1.4), 181 (196-CH_3, 1.5), 167 (181-CH_2, 1.5), 111 (18.4), 84 (C_6H_{12}, 75.5), 83 (74.6), 69 (84-CH_3, 50.3), 57 ($(CH_3)_3C$, 100), 55 (42), 41 (92.2). Anal. Calc. for ($C_{17}H_{28}O_4$): C, 68.87; H, 9.56. Found: C, 68.76; H, 9.67.

(1*R*,4*S*,5*S*)-4-acetyloxymethyl-5-methyl-3-oxabicyclo[3.2.0]heptan-2-one 28 and (1*S*,4*S*,5*R*)-4-acetyloxymethyl-5-methyl-3-oxabicyclo[3.2.0]heptan-2-one 29

A solution of **3g** (148 mg, 0.87 mmol) in freshly distilled acetone (45 mL) was irradiated through pyrex at -45 ° C with introduction of ethylene until the conversion was complete (glc, 5h). The solvent was removed at reduced pressure and the crude was chromatographed on silica gel using a mixture 1:1.5 of ether/hexanes as eluent.

The first fraction gave **29** (51 mg, 30% yield); $[\alpha]_D^{27}$: +83.87 ° (*c* 0.62, $CHCl_3$); ^{1}H-NMR (250 MHz, benzene-d_6) δ 0.7 (s, 3H, CH_3-C), 1.02 (m, 1H), 1.71 (s, 3H, $C\underline{H}_3$-CO), 1.7-1.9 (m, 3H), 2.12 (m, 1H, H-1), 3.8 (dd, $J_{4,8a}$: 8.05 Hz, $J_{4,8b}$: 3.6 Hz, 1H, H-4), 3.95 (dd, J_{gem}: 12.4 Hz, $J_{8b,4}$: 3.6 Hz, 1H, H-8b), 4.09 (dd, J_{gem}: 12.4 Hz, $J_{8a,4}$: 8.04 Hz, 1H, H-8a); ^{1}H-NMR (250 MHz, $CDCl_3$) δ 1.35 (s, 3H, $C\underline{H}_3$-C), 1.7 (dddd, J_{gem}: 11.3 Hz, $J_{6,7}$: 9.5 Hz, $J_{6,7'}$: 3.6 Hz, $J_{6,1}$: 3.6 Hz, 1H, H-6), 2.01 (dddd, J_{gem}: 11.3 Hz, $J_{7',6'}$: 8.7 Hz, $J_{7',6}$: 3.6 Hz, $J_{7',1}$: 2.9 Hz, 1H, H-7'), 2.08 (s, 3H, $C\underline{H}_3$-CO), 2.35 (ddd, J_{gem}: 11.3 Hz, $J_{6',7}$: 9.5 Hz, $J_{6',7'}$: 8.7 Hz, 1H, H-6'), 2.48 (dddd, J_{gem}: 11.3 Hz, $J_{7,6}$: 9.5 Hz, $J_{7,6'}$: 9.5 Hz, $J_{7,1}$: 9.5 Hz, 1H, H-7), 2.70 (ddd, $J_{1,7}$: 9.5 Hz, $J_{1,6}$: 3.6 Hz, $J_{1,7'}$: 2.9 Hz, 1H, H-1), 4.20 (m, 3H, H-8a, H-8b and H-4); ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ 20.5 (CH_2), 20.7 (CH_3), 21.05 (CH_3), 25.5 (CH_2), 43.6 (C, C-5), 44.2 (CH, C-1), 62.5 (CH_2, C-8), 83.7 (CH, C-4), 170.6 (C=O, $CH_3\underline{C}O$), 179.0 (C=O, C-

2); IR (film) ν 2956, 1781 ($\nu_{C=O}$), 1744 ($\nu_{C=O}$), 1370, 1292, 1238, 1182, 1155, 1083, 1047 cm^{-1}; Ms m/z (%) 170 (M$^+$-CH$_2$=CH$_2$, 3), 156 (2), 140 (17), 125 (36), 110 (14), 98 (37), 81 (43), 69 (19), 55 (20), 43 (100). Anal. Calc. for ($C_{10}H_{14}O_4$): C, 60.58; H, 7.12. Found: C, 60.75; H, 6.99.

The second fraction gave **28** (61 mg, 35% yield) as a colorless needles; mp 47-49 °C (ether-pentane); $[\alpha]_D^{27}$: -12.5 ° (*c* 0.48, CHCl$_3$); ^{1}H-NMR (250 MHz, CDCl$_3$) δ 1.31 (s, CH$_3$, Me-cyclobutane), 1.9 (dddd, J_{gem}: 11.7 Hz, $J_{6',7}$: 9.5 Hz, $J_{6',1}$: 3.6 Hz, $J_{6',7}$: 2.9 Hz, 1H, H-6'), 2.05 (s, CH$_3$, 3H, Me-C=O), 2.08 (dddd, J_{gem}: 11.7 Hz, $J_{7,6}$: 9.5 Hz, $J_{7,6'}$: 2.9 Hz, $J_{7,1}$: 2.2 Hz, 1H, H-7), 2.3 (ddd, J_{gem}: 11.7 Hz, $J_{6,7}$: 9.5 Hz, $J_{6,7'}$: 8.7 Hz, 1H, H-6), 2.52 (dddd, J_{gem}: 11.7 Hz, $J_{7',6}$: 9.5 Hz, $J_{7',6}$: 8.7 Hz, $J_{7',1}$: 8.7 Hz, 1H, H-7'), 2.68 (ddd, $J_{1,7'}$: 8.7 Hz, $J_{1,6'}$: 2.9 Hz, $J_{1,7}$: 2.2 Hz, 1H, H-7), 4.01 (dd, J_{gem}: 12.1 Hz, $J_{8a,4}$: 3.6 Hz, 1H, H-8a), 4.3 (dd, J_{gem}: 12.1 Hz, $J_{8b,4}$: 3.6 Hz, 1H, H-8b), 4.39 (dd, $J_{4,8a}$: 3.6 Hz, $J_{4,8b}$: 3.6 Hz, 1H, H-4); ^{13}C-NMR (62.5 MHz, CDCl$_3$) δ 17.9 (CH$_3$, Me-cyclobutane), 20.6 (CH$_3$, CH$_3$CO), 21.3 (CH$_2$), 32.1 (CH$_2$), 43.4 (C, C-5), 43.6 (CH, C-1), 63.3 (CH$_2$), 83.7 (CH, C-4), 170.2 (C=O), 179.7 (C-2); IR (film) ν 2958, 2875, 1779 ($\nu_{C=O}$), 1746 ($\nu_{C=O}$), 1383, 1300, 1235, 1164, 1145, 1070, 1043 cm^{-1}; Ms m/z (%) 199 (M$^+$+1, 2), 171 (1), 170 (M$^+$-28, 4), 156 (3), 140 (18), 125 (36), 98 (32), 81 (72), 69 (20), 55 (19), 43 (100). Anal. Calc. for ($C_{10}H_{14}O_4$): C, 60.58; H, 7.12. Found: C, 60.66; H, 7.13.

(-)-(1*R*,4*S*,5*S*)-5-methyl-4-pivaloyloxymethyl-3-oxabicyclo[3.2.0]heptan-2-one 24 and (+)-(1*S*,4*S*,5*R*)-5-methyl-4-pivaloyloxymethyl-3-oxabicyclo[3.2.0]heptan-2-one 25

A solution of **3e** (105 mg, 0.50 mmol) in freshly distilled acetone (40 mL) was irradiated through pyrex at -45 ° C with introduction of ethylene until the conversion was complete (glc, 3h). The solvent was removed at reduced pressure and the crude was chromatographed on silica gel (0→15% ethyl acetate in hexane as eluent).

The first fraction gave **25** (32 mg, 27% yield) as an oil; bp:105 °C/0.03 Torr; $[\alpha]_D^{20}$: +77.07° (*c* 2.05, CHCl$_3$); ^{1}H-NMR (400 MHz, CDCl$_3$) δ 1.05 (s, 9H, (CH$_3$)$_3$C), 1.48 (s, 3H, CH$_3$-5), 1.72 (dddd, J_{gem}: 12.2 Hz, $J_{6b,7b}$: 9.6 Hz, $J_{6b,7a}$: 3.5 Hz, $J_{6b,1}$: 3.1 Hz, 1H, H-6b), 2.02 (dddd, J_{gem}: 11.9 Hz, $J_{7a,6b}$: 9.3 Hz, $J_{7a,6b}$: 3.5 Hz, $J_{7a,1}$: 2.7 Hz, 1H, H-7a), 2.35 (ddd, J_{gem}: 12.2 Hz, $J_{6a,7a}$: 9.3 Hz, $J_{6a,7b}$: 9.1 Hz, 1H, H-6a), 2.46 (ddd, J_{gem}: 11.9 Hz, $J_{7b,6b}$: 9.6 Hz, $J_{7b,1}$: 9.1 Hz, $J_{7b,6a}$: 9.1 Hz, 1H, H-7b), 2.70 (ddd, $J_{1,7b}$: 9.1 Hz, $J_{1,6b}$: 3.1 Hz, $J_{1,7a}$: 2.7 Hz, 1H, H-1), 4.20 (m, 3H, H-4, H-8a, H-8b); ^{1}H-NMR (400 MHz, benzene-d$_6$) δ 0.7 (s, 3H, CH$_3$-5), 0.95 (m, 1H), 1.3 (s, 9H, (CH$_3$)$_3$C), 1.65-1.80 (m, 3H), 2.10 (m, 1H), 3.63 (dd, $J_{4,8b}$: 7.8 Hz, $J_{4,8a}$: 3.8 Hz, 1H, H-4), 3.90 (dd, J_{gem}: 12.2 Hz, $J_{8a,4}$: 3.8 Hz, H-8a), 4.10 (dd, J_{gem}: 12.2 Hz, $J_{8b,4}$: 7.8 Hz, H-8b); ^{13}C-NMR (20 MHz, CDCl$_3$) δ 20.4 (CH$_2$, C-6), 21.3 (CH$_3$, C-12), 25.5 (CH$_2$, C-7), 27.1 (CH$_3$, C-11), 38.7 (C, C-10), 43.6 (C, C-5), 44.4 (CH, C-1), 62.5 (CH$_2$, C-8), 83.8 (CH, C-4), 178.1 (C-9), 180.0 (C-2); IR (film) ν 2962, 2932, 2873, 1782 ($\nu_{C=O}$), 1732 ($\nu_{C=O}$), 1479, 1457, 1394, 1371, 1281 , 1262, 1149, 1079, 1048, 923, 799 cm^{-1}; Ms m/z (%) 241 (M$^+$+1, 2.5), 156 (0.7), 139 (M$^+$-(CH$_3$)$_3$CCO$_2$, 2.5), 138 (7.3), 125 (4.6), 110 (138-C$_2$H$_4$, 20.5), 98 (4.2), 95 (7.1), 81 (35.4), 68 (17.5), 57 ((CH$_3$)$_3$C, 81.6), 55 (35.8), 41 (100). Anal. Calc. for ($C_{13}H_{20}O_4$): C, 64.98; H, 8.39. Found: C, 64.93; H, 8.51.

The second fraction gave **24** (52 mg, 43% yield) as colorless needles; mp: 61-62 °C (ether-hexane); $[\alpha]_D^{20}$: -18.55° (*c* 1.33, CHCl$_3$); ^{1}H-NMR (400 MHz, CDCl$_3$) δ 1.08 (s, 9H, (CH$_3$)$_3$C), 1.29 (s, 3H, CH$_3$-5), 1.85 (dddd, J_{gem}: 12.1 Hz, $J_{6a,7a}$: 9.8 Hz, $J_{6a,7b}$: 3.4 Hz, $J_{6a,1}$: 3.3 Hz, 1H, H-6a), 2.00 (dddd, J_{gem}: 12.0 Hz, $J_{7b,6b}$: 9.4 Hz, $J_{7b,6a}$: 2.2 Hz, $J_{7b,1}$: 2.1, H-7b), 2.27 (ddd, J_{gem}: 12.1 Hz, $J_{6b,7b}$: 9.4 Hz, $J_{6b,7a}$: 9.2 Hz, 1H, H-6b), 2.48 (dddd, J_{gem}: 12.0 Hz, $J_{7a,6a}$: 9.8 Hz, $J_{7a,1}$: 9.6 Hz, $J_{7a,6b}$: 9.2 Hz, 1H, H-7a), 2.66 (ddd, $J_{1,7a}$: 9.6 Hz, $J_{1,6b}$: 3.3 Hz, $J_{1,7b}$: 2.1 Hz, 1H, H-1), 3.96 (dd, J_{gem}: 12.4 Hz, $J_{8a,4}$: 2.3 Hz, 1H, H-8a), 4.23 (dd, J_{gem}: 12.4 Hz, $J_{8b,4}$: 3.0 Hz, 1H, H-8b), 4.34 (dd, $J_{4,8b}$: 3.0 Hz, $J_{4,8a}$: 2.3 Hz, 1H, H-4); ^{13}C-NMR (20 MHz, CDCl$_3$) δ 17.8 (CH$_3$, C-12), 21.2 (CH$_2$, C-6), 27.0 (CH$_3$, C-11), 32.2 (CH$_2$, C-7), 38.6 (C, C-10), 43.3 (C, C-5), 43.8 (CH, C-1), 63.2 (CH$_2$, C-8), 83.9 (CH, C-4), 177.6 (C-9), 179.5 (C-2); IR (film) ν 2972, 2875, 1779 ($\nu_{C=O}$), 1734 ($\nu_{C=O}$), 1479, 1457, 1396, 1338, 1282, 1148, 1043, 960 cm^{-1}; Ms m/z (%) 241 (M$^+$+1, 4.8), 227 (M$^+$+1 -CH$_2$, 0.2), 139 (M$^+$-(CH$_3$)$_3$CCO$_2$, 2.4), 138 (9.4), 125 (13), 110 (138-C$_2$H$_4$, 10.5), 98 (12.7), 81 (53.8), 68 (16.9), 57 ((CH$_3$)$_3$C, 81.4), 55 (30), 41 (100). Anal. Calc. for ($C_{13}H_{20}O_4$): C, 64.98; H, 8.39. Found: C, 64.95; H, 8.42.

(-)-(1*R*,2*R*,5*S*)-2-phenyl-3,6-dioxabicyclo[3.2.1]heptan-7-one, 39

A solution of **3h** (150 mg, 0.74 mmol) in freshly distilled acetone (45 mL) was irradiated at -7 °C for 40' through quartz and for 3 h through pyrex under Ar atmosphere. The solvent was removed at reduced pressure and the crude was chromatographed on silica gel (0→25% ethyl acetate in hexane as eluent) to afford **39** (78 mg, 52% yield) as a colorless crystalline solid; mp: 112-114 °C (ethyl acetate-hexane); $[\alpha]_D^{20}$: -114.55° (*c* 1.15, $CHCl_3$); ^{1}H-NMR (400 MHz, benzene-d_6) δ 1.36 (d, J_{gem}: 11.7 Hz, 1H, H-8a), 1.56 (dt, J_{gem}: 11.7 Hz, $J_{8b,1}$: 5.85 Hz, $J_{8b,5}$: 5.8 Hz, 1H, H-8b), 2.74 (ddd, $J_{1,8b}$ 5.8 Hz, $J_{1,2}$: 2.1 Hz, $J_{1,8a}$: 1.2 Hz, 1H, H-1), 3.20 (dd, J_{gem}: 11.9 Hz, $J_{4b,5}$: 2.1 Hz, 1H, H-4b) 3.61 (ddd, J_{gem} 11.9 Hz, $J_{4a,8b}$: 2.4 Hz, $J_{4a,5}$: 2.1 Hz, , 1H, H-4a), 3.81 (ddd, $J_{5,8b}$: 5.8 Hz, $J_{5,4a}$: 2.1 Hz, $J_{5,4b}$: 2.1 Hz, 1H, H-5), 5.30 (d, $J_{2,1}$: 2.1 Hz, 1H, H-2); ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ 170.1 (C=O), 129.7, 128.9, 128.5, 127.7, 125.5, 76.3 (CH, C-2), 74.2 (CH, C-5), 64.2 (CH_2, C-4), 43.5 (C-1), 29.9 (CH_2, C-8); IR (KBr) ν 2256, 1785 ($\nu_{C=O}$), 1454, 1352, 1159, 1025, 990, 906, 737 cm^{-1}; Ms m/z (%) 204 (M^+, 33), 160 (M^+-CO_2, 3), 149 (10), 129 (160-CH_2OH, 5), 115 (47), 91 ($CH_2C_6H_5$, 100), 77 (C_6H_5, 46), 55 (78), 51 (41). Anal. Calc. for ($C_{12}H_{12}O_3$) C, 69.57; H, 5.92. Found: C, 69.38; H, 5.87.

(-)-(*1S,4S,5S,6S,7R*)-6,7-carbonyldioxy-4-pivaloyloxymethyl-3-oxabicyclo[3.2.0]heptan-2-one, 30 and (*1R,4S,5R,6R,7S*)-6,7-carbonyldioxy-4-pivaloyloxymethyl-3-oxabicyclo[3.2.0]heptan-2-one, 31.

A solution of **3d** (136 mg, 0.69 mmol) and vinylene carbonate (0.17 mL, 2.75 mmol) in freshly distilled acetone (45 mL) was irradiated at -77 °C for 4h through pyrex under Ar atmosphere. The solvent was removed at reduced pressure and the crude was chromatographed on silica gel (0→20% ethyl acetate in hexane as eluent).

The first fraction gave **31** (14 mg, 7.1% yield) as a colorless solid; mp: 162-163 °C (ethyl acetate-hexane); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.20 (s, 9H, $(CH_3)_3C$), 3.46 (ddd, $J_{5,1}$: 8.04 Hz, $J_{5,4}$: 5.85 Hz, $J_{5,6}$: 2.93 Hz, 1H, H-5), 3.67 (d, $J_{1,5}$: 8.04 Hz, 1H, H-1), 4.39 (dd, J_{gem}: 12.43 Hz, $J_{8a,4}$: 5.85 Hz, 1H, H-8a), 4.45 (dd, J_{gem}: 12.43 Hz, $J_{8b,4}$: 5.85 Hz, 1H, H-8b), 4.85 (ddd, $J_{4,8a}$: 5.85 Hz, $J_{4,8b}$: 5.85 Hz, $J_{4,5}$: 5.85 Hz, 1H, H-4), 5.10 (d, $J_{7,6}$: 5.85 Hz, 1H, H-7), 5.30 (dd, $J_{6,7}$: 5.85 Hz, $J_{6,5}$: 2.93 Hz, 1H, H-6); ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ 177.7, 171.7, 154.2, 76.9, 74.3, 61.4 (CH_2), 46.2, 45.0, 38.8, 29.6, 27.0 ($(CH_3)_3$); IR (KBr) ν 2925, 1827 ($\nu_{C=O}$), 1775 ($\nu_{C=O}$), 1725 ($\nu_{C=O}$), 1152, 1075 cm^{-1}; Ms m/z (%): 303.65 (3), 302.65 (M^++18, 15), 301.60 (M^++17, 100), 284.60 (M^+,1), 273.65 (2).

The second fraction gave **30** (52 mg, 43% yield) as colorless needless; mp: 147-149 °C (ethyl acetate-hexane); $[\alpha]_D^{20}$: -67.50° (*c* 1.20, $CHCl_3$); ^{1}H-NMR (400 MHz, benzene-d_6) δ 1.08 (s, 9H, $(CH_3)_3C$), 2.13 (ddd, $J_{5,1}$: 7.9 Hz, $J_{5,6}$: 2.4 Hz, $J_{5,4}$: 1.2 Hz, 1H, H-5), 2.98 (ddd, $J_{1,5}$: 7.9 Hz, $J_{1,7}$: 1.2 Hz, $J_{1,6}$: 0.9 Hz, 1H, H-1), 3.28 (dd, J_{gem}: 12.2 Hz, $J_{8a,4}$: 3.6 Hz, 1H, H-8a), 3.51 (ddd, $J_{4,8a}$: 3.6 Hz, $J_{4,8b}$: 3.05 Hz, $J_{4,5}$: 1.2 Hz, 1H, H-4), 3.65 (ddd, $J_{6,7}$: 5.5 Hz, $J_{6,5}$: 2.4 Hz, $J_{6,1}$: 0.9 Hz, 1H, H-6), 3.80 (dd, J_{gem}: 12.2 Hz, $J_{8b,4}$: 3.05 Hz, 1H, H-8b), 4.15 (dd, $J_{7,6}$: 5.5 Hz, $J_{7,1}$: 1.2 Hz, 1H, H-7); ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ 177.6, 172.0, 154.2, 79.1 (CH), 78.2 (CH), 77.4 (CH), 65.0 (CH_2), 46.0 (CH), 45.1 (CH), 38.8, 27.0 ($(CH_3)_3$); IR (KBr) ν 2973, 1806 ($\nu_{C=O}$), 1785 ($\nu_{C=O}$), 1735 ($\nu_{C=O}$), 1370, 1349, 1278, 1180, 1138, 1089 cm^{-1}; Ms m/z (%) 303.65 (3), 302.65 (M^++18, 16), 301.65 (M^++17, 100), 284.60 (M^+, 2), 241.80 (1). Anal. Calc. for ($C_{13}H_{16}O_7$): C, 54.93; H, 5.67. Found: C, 54.98; H, 5.81.

(1*S*,4*S*,5*S*,6*S*,7*R*)-6,7-carbonyldioxy-5-methyl-4-pivaloyloxymethyl-3-oxabicylo[3.3.0]-heptan-2-one, 32 and (1*S*,4*R*,5*R*,6*R*,7*S*)-6,7-carbonyldioxy-5-methyl-4-pivaloyloxymethyl-3-oxabicyclo[3.3.0]heptan-2-one, 33.

A solution of **3e** (145 mg, 0.67 mmol) and vinylene carbonate (0.21 mL, 3.35 mmol) in freshly distilled acetone (50 mL) was irradiated at -77 °C for 6h through pyrex under Ar atmosphere. The solvent was removed at reduced pressure and the crude was chromatographed on silica gel (0→20% ethyl acetate in hexane as eluent).

The first fraction gave **33** (13 mg, 6.4% yield) as a colorless solid; mp: 203-204 °C (ethyl acetate-hexane); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.19 (s, 9H, $(CH_3)_3C$), 1.45 (s, 1H, CH_3), 3.26 (s, 1H, H-1), 4.38 (dd, J_{gem}: 12.8 Hz, $J_{8a,4}$: 5.6 Hz, 1H, H-8a), 4.38 (dd, J_{gem}: 12.8 Hz, $J_{8b,4}$: 6.2 Hz, 1H, H-8b), 4.51 (dd, $J_{4,8b}$: 6.2 Hz, $J_{4,8a}$: 5.6 Hz, 1H, H-4), 5.04 (d, $J_{6,7}$: 5.5 Hz, 1H, H-6), 5.25 (d, $J_{7,6}$: 5.5 Hz, 1H, H-7); ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ 177.6, 171.3, 154.3, 82.8, 76.0, 75.0, 60.9, 50.8, 48.9, 38.7, 26.9, 17.0; IR (film) ν 2987, 1841 ($\nu_{C=O}$), 1778 ($\nu_{C=O}$), 1736 ($\nu_{C=O}$), 1482, 1356 cm^{-1}; Ms m/z (%) 317 (16), 316 (M^++18, 100), 272 (3), 230 (5), 170 (9), 136 (3), 128 (5), 74 (1). Anal. Calc. for ($C_{14}H_{18}O_7$): C, 56.37; H, 6.08 Found: C, 56.25; H, 5.89.

The second fraction gave **32** (96 mg, 47.5% yield) as colorless needles; mp: 187-188 °C (ethyl acetate-hexane); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.15 (s, 9H, $(CH_3)_3C$), 1.38 (s, 1H, CH_3), 3.20 (s, 1H, H-1), 4.08 (dd, J_{gem}: 12.8 Hz, $J_{8a,4}$: 2.1 Hz, 1H, H-8a), 4.41 (dd, J_{gem}: 12.8 Hz, $J_{8b,4}$: 2.7 Hz, 1H, H-8b), 4.71 (dd, $J_{4,8b}$: 2.7 Hz, $J_{4,8a}$: 2.1 Hz, 1H, H-4), 5.07 (d, $J_{6,7}$: 5.2 Hz, 1H, H-6), 5.12 (d, $J_{7,6}$: 5.2 Hz, 1H, H-7); ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ 177.2, 171.9, 154.4, 82.3, 79.4, 77.4, 62.5, 49.9, 49.0, 38.5, 26.9, 12.4; IR (KBr) ν 2984, 1799 ($\nu_{C=O}$), 1728 ($\nu_{C=O}$), 1173, 1146, 1062, 912 cm^{-1}; Ms m/z (%) 316 (M^{+}+18, 100), 272 (6), 230 (7), 170 (26), 136 (11), 128 (10), 74 (19). Anal. Calc. for ($C_{14}H_{18}O_7$): C, 56.37; H, 6.08. Found: C, 56.27; H, 5.73.

REFERENCES

1. a) Eaton, P.E. *J. Am. Chem. Soc.* 1962, **84**, 2454. b) Corey, E.J.; Bass, J.D.; LeMahieu, R.; Mitra, R.B. *J. Am. Chem. Soc.* 1964, **86**, 5570. c) Corey, E.J.; Mitra, R.B.; Uda, H. *J. Am. Chem. Soc.* 1964, **86**, 485. d) Carless, H.A.J. *Photochemistry in Organic Synthesis*; Coyle, J.D., Ed.; Royal Soc. Chem.: London, 1986; pp 95-117.
2. a) Ohga, K.; Matsuo, T. *Bull. Chem. Soc. Jpn.* 1970, **43**, 3505. b) Tada, M.; Kokubo, T.; Sato, T. *Tetrahedron* 1972, **28**, 2121. c) Ohga, K.; Matsuo, T. *Bull. Chem. Soc. Jpn.* 1976, **49**, 1590. d) Kosuga, H.; Sekiguchi, S.; Sekita, R.; Uda, H. *Bull. Chem. Soc. Jpn.* 1976, **49**, 520. e) Coates, R.M.; Senter, P.D.; Baker, W.R. *J. Org. Chem.* 1982, **47**, 3597.
3. a) Tomioka, K.; Tanaka, M.; Koga, K. *Tetrahedron Lett.* 1982, **23**, 3401. b) Tanaka, M.; Tomioka, K.; Koga, K. *Tetrahedron Lett.* 1985, **26**, 3035. c) Demuth, M.; Palomer, A.; Sluma, H.-D.; Dey, A.K.; Krüger, C.; Tsay, Y.H. *Angew. Chem.* 1986, **98**, 1093. *Angew. Chem. Int. Ed. Engl.* 1986, **25**, 1117. d) Tomioka, K.; Tanaka, M.; Koga, K. *Chem. Pharm. Bull.* 1989, **37**, 1201. e) Hoffmann, N.; Scharf, H.-D.; Runsink, J. *Tetrahedron Lett.* 1989, **30**, 2637. f) Alibés, R.; Bourdelande, J.L.; Font, J. *Tetrahedron: Asymmetry* 1991, **2**, 1391. g) Hoffmann, N.; Buschmann, H.; Raabe, G.; Scharf, H.-D. *Tetrahedron* 1994, **50**, 11167.
4. a) Tumlinson, J.H.; Hardee, D.D.; Gueldner, R.C., Thompson, A.C.; Hedin, P.A. Minyard, J.P. *Science*, 1969, **166**, 1010. b) Tumlinson, J.H.; Gueldner, R.C.; Hardee, D.D.; Thompson, A.C.; Hedin, P.A. Minyard, J.P. *J. Org. Chem.*, 1971, **36**, 2616.
5. a) Mori, K.; Fukamatsu, K. *Libigs Ann. Chem.* 1991, 341. b) Confalonieri, G.; Marotta, E.; Rama, F.; Righi, P.; Rosini, G.; Serra, R.; Venturelli, F. *Tetrahedron* 1994, **50**, 3235.
6. Camps, P.; Cardellach, J.; Font, J.; Ortuño, R.M.; Ponsati, O. *Tetrahedron*, 1982, **38**, 2395.
7. Padwa, A. *1,3-Dipolar Cycloaddition Chemistry* Taylor, E.C.; Weissberger, A. Ed.; Wiley, 1984, vol. 1. pp 359-393.
8. a) Tomioka, K.; Sato, F.; Koga, K. *Heterocycles* 1982, **17**, 311. b) Ortuño, R.M.; Bigorra, J.; Font, J. *Tetrahedron* 1987, **43**, 2199. c) Hannesian, S.; Murray, P.J. *Tetrahedron* 1987, **43**, 5055. d) Feringa, B.L.; De Lange, B.; De Jong, J.C. *J. Org. Chem.* 1989, **54**, 2471.
9. a) Parella, T.; Sánchez-Ferrando, F.; Virgili, A. *Bull. of Magn. Reson.* 1992, **14**, 263. b) Parella, T.; Sánchez-Ferrando, F.; Virgili, A. *J. Magn. Reson. Chem.* 1994, **32**, 343.
10. Breitmeier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy. High-Resolution Methods and Applications in Organic Chemistry and Biochemistry*. VCH, Weinheim, 1987; pp 115 and 185.
11. Loufty, R.D.; de Mayo, P. *J. Am. Chem. Soc.* 1977, **99**, 3559.
12. Schuster, D.I,; Lem, G.; Kapninidis, N.A. *Chem. Rev.* 1993, **93**, 3.
13. Gilchrist, T.L.; Storr, R.C. *Organic Reactions and Orbital Symmetry*, Cambridge University Press, Cambridge, 1972; pp 241-244.
14. Alibés, R.; Bourdelande J.L.; Font, J.; Gregori, A. *J. Braz. Chem. Soc.* 1995, **6**, 119.

(*Received in UK* 31 *July* 1995; *revised* 31 *October* 1995; *accepted* 2 *November* 1995)