Tetrahedron Vol 45, No 14, pp 4565 to 4578, 1989
Printed in Great Britain

0040-4020/89 $3 00+ 00

REGIOSELECTIVE ELECTROPHILIC ADDITIONS TO 2-OXYGENATED-7-OXABICYCLO[2.2.1]HEPT-5-ENES: A SIMPLE ENTRY INTO THE 4,7-DIOXATRICYCLO[3.2.1.$0^{3,6}$]OCTANE SKELETON[1]

ODON ARJONA[a], ROBERTO FERNANDEZ DE LA PRADILLA[b], JOAQUIN PLUMET*[c] AND ALMA VISO[a].

a) Departamento de Química Orgánica, Facultad de Química, Universidad Complutense, 28040 Madrid, Spain. b) Instituto de Química Orgánica, C.S.I.C., Juan de la Cierva 3, 28006 Madrid, Spain. c) Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Extremadura, Avda de Elvas S/N, 06071 Badajoz, Spain.

(*Received in UK* 24 *April* 1989)

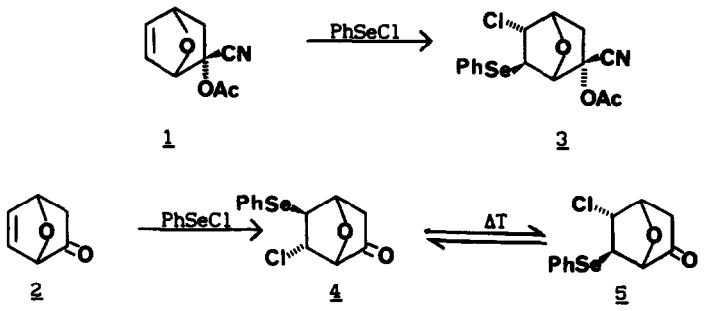
Abstract- The regio- and stereoselectivity of the reaction between PhSeCl and PhSCl and a number of 7-oxabicyclo[2.2.1]hept-5-enes bearing an oxygenated substituent on C-2 is discussed. In most cases, both electrophiles react with complete regio- and stereoselectivity to provide 5-*endo*-chloro- 6-*exo*-benzeneselenenyl (benzenesulfenyl) derivatives. 7-Oxanorbornen- 2-*endo*-ols behave differently with both electrophiles. Thus, while PhSeCl produces 5-*endo*-chloro-6-*exo*-benzeneselenenyl adducts and small amounts of 4,7- dioxatricyclo[3.2.1.$0^{3,6}$]octane derivatives, PhSCl affords a good yield of 5-*exo*-methyl-2-*exo*-phenylsulfenyl-4,7-dioxatricyclo [3.2.1.$0^{3,6}$]octane.

The chemistry of derivatives of 7-oxabicyclo[2.2.1]heptane has attracted a great deal of attention in the past few years[2], especially due to the wide range of natural products and compounds of biological interest accessible from such substrates[3]. Within this context, oxanorbornenic substrates 1 and 2 (Scheme I) are particularly versatile starting materials for the preparation of a variety of natural products[4]. Furthermore, these synthetic intermediates ("naked sugars"[4a]) are now readily available[5] even optically pure.[6]

Scheme I illustrates a remarkable feature of oxabicyclic olefins 1 and 2, namely the completely regio- and stereoselective electrophilic addition of soft electrophiles (PhSeX, ArSCl) under kinetic control to afford the corresponding adducts 3 and 4[7]. The remote control of the reaction by the substituents at C-2 has been attributed to homoconjugative and/or hiperconjugative effects. This methodology has been successfully applied to the synthesis of L-Daunosamine[4a].

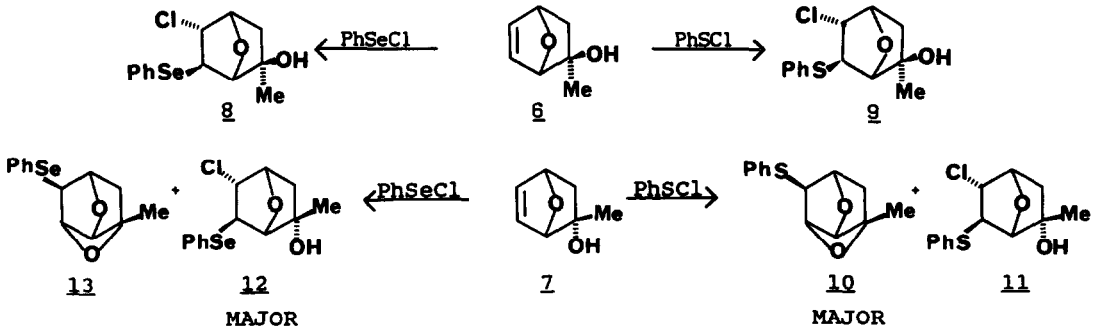
During the past several years we have been engaged in the study of new aspects of the reactivity of these systems[8]. In this context, we have explored the electrophilic additions of PhSeCl and PhSCl to a variety of 7-oxanorbornenic substrates bearing an oxygenated substituent on C-2. The results obtained in the course of these studies are disclosed in this report.

Scheme I



The initial stage of our investigation[1] addressed the influence, if any, of the stereochemistry of the substituents at C-2 on the outcome of these electrophilic additions. The readily available methyl carbinols 6 and 7[8b] were considered to be appropiate substrates for this purpose. Furthermore, an appealing feature of these bicyclic olefins was that their electronic characteristics were sufficiently different from those of cyanoacetoxy derivative 1 and ketone 2, and this would further define the scope of these stereoselective additions[7].The results obtained for 6 and 7 are shown in Scheme II.

Scheme II

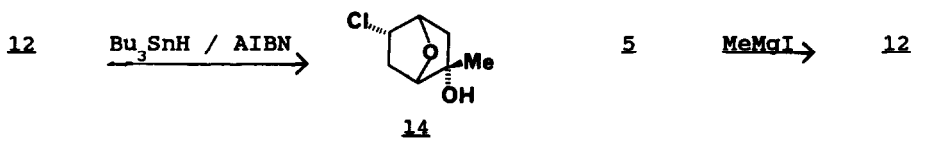


When *exo* isomer 6 was treated with PhSeCl and PhSCl, the corresponding adducts, 8 and 9, were obtained in good yields. The reaction proceeded in a

totally regio- and stereoselective manner by electrophilic *exo* attack and subsequent *endo* addition of the nucleophile on C-5, as observed for cyanoacetoxy derivative 1[7]. However, *endo* isomer 7 afforded different results for both electrophiles, as indicated in Scheme II. While treatment with the harder electrophile PhSCl led to a good yield of the unexpected tricyclic oxetane 10, and a small amount of 11, the reaction with PhSeCl produced adduct 12 and small amounts of seleno oxetane 13. It should be pointed out that, to the best of our knowledge, 13 is the first case known of an intramolecular phenylselenoetherification. The structure of phenylseleno carbinol 12 was confirmed by chemical means, as shown bellow.

Adduct 12 presented H-5 and H-6 remarkably deshielded (0.77-0.90 ppm) relative to 8 or 3[7]; this was mistakenly attributed to a reversal of the regio- and stereoselectivity of the reaction to produce the corresponding 6-*exo*-chloro-5-*endo*-phenylselenenyl derivative[9,10,11]. In order to conclusively prove the structural assignment for 12 we effected some transformations indicated in Scheme III. The first transformation explored was the deselenation of 12 with Bu_3SnH which afforded chlorocarbinol 14 whose spectral data was consistent with the proposed structure. Furthermore, nucleophilic addition of MeMgI to ketone 5, prepared by methanolysis of 3[4a], led to a product of structure 12, by *exo* attack[12]. The spectral features of this compound turned out to be identical to those of the product of direct addition of PhSeCl to 7. We truly regret having effected this mistaken assignment and the inconveniences it might have caused. Nevertheless, this unusually high deshielding observed for 12 relative to 8 is quite surprising since, generally, the shielding or deshielding effects of a hydroxyl and a methyl group are quite similar[13]. This observation may be attributed to a close proximity between H-6 and the oxygenated substituent[14].

Scheme III



14

The unexpected results described above prompted us to examine these processes in more detail. It was considered that the behavior of other oxanorbornenic substrates bearing an endo oxygenated functionality at C-2 should be examined since, the electronic features of 6 and 7 were perceived to be quite different from those of cyanoacetoxy substrate 1 and, nevertheless, identical regio- and stereochemical results had been encountered. The substrates selected for this study are indicated in Scheme

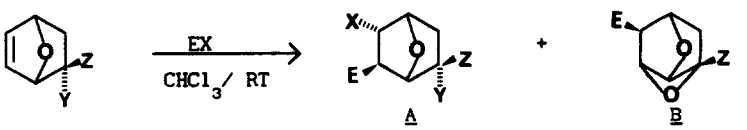
IV. Oxanorbornene derivatives 15-18 were readily available[8] and their substituents on C-2 presented fairly different electronic characteristics. For the sake of clarity those processes that resulted in the formation of tricyclic oxetanes analogous to 10, will be discussed separately.

Scheme IV

15 16 17 18

β-Lactones 15 and 16 produced good yields of adducts 19-23, as indicated in Table I (entries 4-8), whose structure was deduced from their spectral data (^{1}H NMR) in good agreement with literature values[7], perhaps with the exception of H-6 which resonated 0.2-0.3 ppm downfield from the usual values. This small shift was attributed to the presence of a strained β-lactone funcionality which may distort the bicyclic system. Diol 17, on

Table I. Reaction between 2-Oxygenated-7-oxanorbornenes and PhSeCl, PhSeBr and PhSCl.



A B

entry	substr[a].	EX	A(yield %)[b]	B(yield %)
1	6	PhSeCl	8(75)	
2	6	PhSCl	9(78)	
3	7	PhSeCl	12(65)	13(16)[c]
4	15	PhSeCl	19(74)	
5	15	PhSCl	20(63)	
6	16	PhSeCl	21(62)	
7	16	PhSCl	22(55)	
8	16	PhSeBr	23(78)	
9	17	PhSeCl	24(62)	25(12)[c]
10	18	PhSeCl	complex mixture of products	

[a] 6: Z= OH, Y= Me; 7: Z= Me, Y= OH; 15: Z= Y= (*endo*-O-)-O-CO-CCl_2-; 16: Z= Y= (*endo*-O-)-O-CO-CH_2-; 17: Z= -CH_2-CH_2-OH, Y= OH; 18: Z= Ph, Y= OH

[b] Yields of pure products.

[c] Yield determined by integration of the ^{1}H NMR spectrum of the crude reaction mixture.

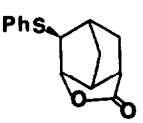
the other hand, afforded 24 and a small amount (12%) of oxetane 25 (Table I, entry 9), as in the addition of PhSeCl to *endo* methyl carbinol 7 (Table I, entry 3). The structure of 24 was confirmed by reductive opening of β-lactone 21 which yielded a diol of identical spectral features to the product of direct addition of PhSeCl to diol 17. Surprisingly, the reaction of phenyl carbinol 15 with PhSeCl (entry 10) led to a complex reaction mixture from which no addition or cyclization products could be isolated.

The high regioselectivity encountered in the electrophilic additions to 7 and 15-17 (Table I) may be related to an electrostratic effect of the *endo*-O-atom[11a]. However, this rationalization fails to account for the regioselectivity of additions to *exo*-carbinol 6 which may be attributed to steric hindrance by the *endo* methyl substituent. These results indicate that there must be a delicate interplay of several factors controlling these electrophilic additions. Undoubtedly, more data is needed to further clarify the relative importance of these factors.

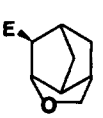
Synthesis of Derivatives of 4,7-Dioxatricyclo[3.2.1.$0^{3,6}$]octane

Phenylsulfenolactonizations and phenylselenoetherifications of norbornenic substrates to produce tricyclic derivatives such as 26[15] and 27[16](Scheme V) are well known. In 1985, norbornenic oxetane 28 was prepared by sequential reaction of the corresponding alcohol with *n*-BuLi and PhSCl, presumably via an intermediate sulfenate ester[17].On the other hand, 29 was recently described as an example of a general method of sulfenoetherification (PhSCl/i-Pr_2NEt)[18,19]. In 1988, Le Drian and Vogel[10] reported the synthesis of (+)-1,3:2,5-Dianhydroviburnitol, 30, by means of a base induced intramolecular epoxide opening of the correponding epoxy-*endo*-alcohol[20]. Derivatives of 30 are efficient herbicides and plant-growth regulators[21].

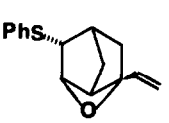
Scheme V



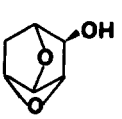
26



27 (E= PhSe)
29 (E= PhS)



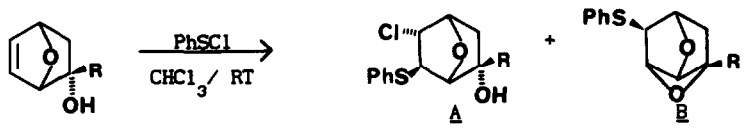
28



30

In the initial stage of our investigation[1] we found that the treatment of *endo* carbinol 7 with PhSCl in $CHCl_3$ at room temperature afforded a good yield of tricyclic oxetane 10, along with small amounts of the addition product 11 (Table II). Phenyl carbinol 18, on the other hand, led to a

Table II. Reaction between 7-Oxanorbornen-2-*endo*-ols and PhSCl

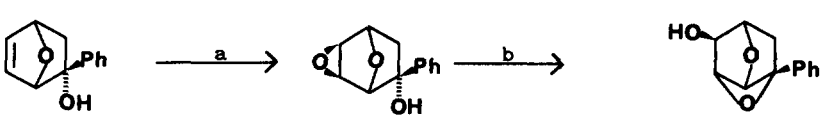


entry	substr.(R)	A	B	ratioA/B
1	7 (Me)	11	10	1:4
2	18 (Ph)	complex mixture of products		
3[a]	7 (Me)	11	10	1:2.5
4[b]	7 (Me)	11	10	1:2.0
5[c]	7 (Me)	11	10	3:1
6[d]	7 (Me)	11	10	2.5:1
7[e]	7 (Me)	11	10	1:2.4
8[f]	7 (Me)	11	10	1.1:1
9[g]	7 (Me)	11	10	2.5:1

[a]The reaction was carried out in CH_3CN.
[b]The reaction was carried out in CCl_4.
[c]The reaction was carried out in Et_2O.
[d]The reaction was carried out in THF.
[e]The reaction was carried out in the presence of 2.2 equiv. of i-Pr_2NEt in CH_3CN.
[f]The reaction was carried out on the lithium alkoxide (2 + MeLi) in Et_2O.
[g]The reaction was carried out on the lithium alkoxide (2 + MeLi) in THF.

complex reaction mixture from which no oxetane or addition products could be isolated. This substrate appeared to be especially prone to afford decomposition products instead of the expected oxetane. In order to ascertain wether or not this was due to an intrinsic lack of stability of an oxetane functionality in this case (Table II, B, R= Ph), we prepared the structurally related hydroxy oxetane 32 by a base induced epoxide opening of 31[20] which in turn was prepared by mCPBA epoxidation of 17 (Scheme VI).

Scheme VI[a]



17 31 32

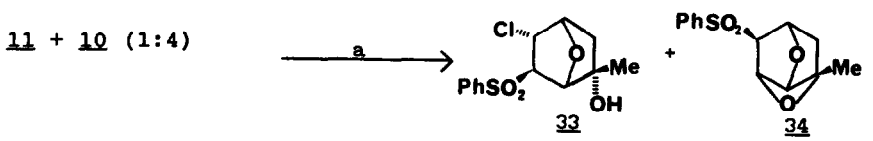
[a]Reagents: (a) mCPBA, $CHCl_3$, 24 h, 92%; (b) t-BuOK, THF, 0°C, 15 min, 78%

The straightforward preparation of hydroxy oxetane 32 indicates that the results encountered for the electrophilic addition of PhSCl to 18 (and presumably, for PhSeCl as well, Table I) are related with the reaction conditions and not with the lack of stability of the phenylsulfenyl analog of 32.

The unexpected intramolecular cyclization without any added base to produce oxetane 10 led us to investigate a variety of different reaction conditions (entries 3-9). The effect of the solvent was examined first (entries 1, 3-6) and $CHCl_3$ was found to produce the best yield of cyclized product while, remarkably, the major product in EtO_2 and THF was adduct 11. Addition of PhSCl to a mixture of 7 and 2.2 equiv of i-Pr_2NEt in CH_3CN (entry 7) did not result in any significant increase of the cyclization. Entries 8 and 9 indicate that no improvement in the cyclization could be realized by effecting the reaction on the preformed lithium alkoxide derived from 7[12] with respect to the result shown in entry 1.

The oxidation of the phenylsulfenyl moiety of this system to a sulfone functionality was addressed, both as a preliminary exploration into the reactivity of these derivatives and as an additional means to secure the stereochemical assignment of this oxetane (vide infra). Thus, the reaction of the crude mixture of 11 and 10 (1:4 ratio) with mCPBA in the presence of solid K_2CO_3 afforded a good yield of hydroxy sulfone 33 and tricyclic sulfone 34, readily separated by fractional recrystallization (Scheme VII).

Scheme VII

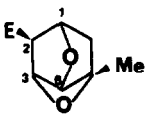


(a) mCPBA, K_2CO_3, CH_2Cl_2, 82%

The structural assignment for these oxetanes was derived from their spectral data, especially from their ^{1}H NMR spectra with the help of selective decoupling techniques and a NOE measurement (see experimental) Table III contains selected ^{1}H NMR data for these systems. The coupling patterns for H-6 (d) and H-1 (d), with small long range couplings, determine the stereochemistry of the substituents on C-2 and C-3. The strong deshielding observed for H-6 (with respect to bicyclic derivatives) is consistent with a strained oxetane functionality; this strain may account for the fact that H-2 appears as a singlet. The spectral data measured are

consistent with those found in the literature for related oxanorbornenic[10] and norbornenic[17,18,22,23] analogs. Sulfone 34 presented H-1 and H-3 considerably deshielded relative to sulfide 10; this is consistent with a *syn* stereochemisty for these protons and the sulfone moiety and supports the proposed structure.

Table III. Selected ^{1}H NMR Data for Tricyclic Oxetanes 10 and 34[a]



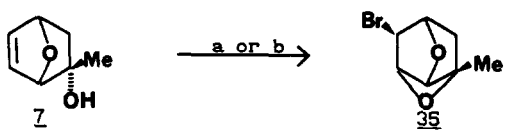
	H-1	H-2	H-3	H-6
10	4.91(dt)	3.65(s)	4.61(dd)	5.07(dd)
34	5.37(ddd)	3.64(s)	5.09(dd)	5.01(dd)

10, E= PhS
34, E= $PhSO_2$

[a]Chemical shifts in δ units downfield from TMS.

The facile phenylsulfenoetherification of 7-oxanorbornen-2-*endo*-ols is unprecedented in the literature. In a related study on the bromination of some oxanorbornenic derivatives[24] we have encountered another unprecedented oxetane forming reaction, indicated in Scheme VIII. In sharp contrast with other oxanorbornenic derivatives for which mixtures of addition and

Scheme VIII



7 35

(a) Br_2 / CCl_4, 95% (b) Br_2 or NBS / CH_2Cl_2 / AcOH / H_2O, 95%

rearrangement products were obtained, *endo*-alcohol 7 led to bromo oxetane 35 in essentially quantitative yields. This bromoetherification, which does not take place in norbornenic substrates[22], is another example of the differences in reactivity encountered many times for oxanorbornenic derivatives relative to their norbornenic analogs and shows that *endo*-oxanorbornenic alcohols have a remarkable tendency to undergo intramolecular cyclizations with a variety of electrophiles.

Conclusions

The reaction between a number of 7-oxanorbornenes bearing an oxygenated substituent on C-2 and PhSeCl and PhSCl leads to 5-*endo*-chloro-6-*exo*-benzeneselenenyl (benzenesulfenyl) derivatives. The regioselectivity of the process appears to be controlled by electronic and steric effects. On the other hand, 2-*exo*-methyl-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-ol undergoes an unprecedented and extremely facile sulfenoetherification by reaction with PhSCl to produce a good yield of 5-*exo*-methyl-2-*exo*-phenylsulfenyl-4,7-dioxatricyclo[3.2.1.$0^{3,6}$]octane[25]. Low yields of the

corresponding benzeneselenenyl tricyclic systems are also formed by an unprecedented phenylselenoetherification process.

EXPERIMENTAL

General. All reactions were carried out under a positive pressure of dry nitrogen or argon,using freshly distilled solvents unless otherwise stated. Reagents and solvents were handled by using standard syringe techniques. Diethyl ether and tetrahydrofuran were distilled from lithium aluminum hydride; hexane, ethyl acetate and chloroform from phosphorus pentoxide and methylene chloride from calcium hydride. Commercial methyllithium (low halide solution in ether) was purchased from Aldrich and titrated[26] prior to use. Diisopropylethylamine was purchased from Aldrich and destilled from barium oxide prior to use. mCPBA was purchased from Merck with 15% of m-Chlorobenzoic acid. PhSCl was prepared by the standard literature procedure[27].Analytical TLC was carried out on 0.20 mm E.Merck precoated silica gel plates (60 F-254), with detection by UV light, iodine or acidic vanillin solution. Column chromatography was performed using E. Merck 230-400 mesh or 70-230 mesh silica gel. Melting points were determined on a Büchi 512 apparatus and are uncorrected. Infrared spectra were recorded on either a Perkin Elmer 781 or 257 grating spectrophotometers; band positions are indicated in wavenumbers. ^{1}H NMR spectra were recorded on a Varian T-60A, Brüker AM-200 or Varian XL-300 instrument, using $CDCl_3$ as solvent. ^{13}C NMR spectra were measured on a Varian FT-80-A or Brüker AM-200 instrument, using $CDCl_3$ as solvent, and are completely decoupled. In both, ^{1}H NMR and ^{13}C NMR, chemical shifts are reported in δ units downfield from tetramethylsilane. The following abbreviations are used to describe peak patterns when appropiate: br= broad, s= singlet, d= doublet, t= triplet, tap= apparent triplet q= quartet, m= multiplet[28]. All new compounds described in this report are racemic.

General Procedure for Electrophilic Additions to 7-Oxanorbornenic Systems. To a solution of 1 equivalent of the 7-oxanorbornenic derivative in chloroform (10 ml/mmol) was added a solution of 1.3 equivalent of PhSeCl, PhSeBr or, PhSCl in chloroform (3ml/mmol). The mixture was stirred at room temperature for the time indicated in each case. The mixture was quenched with a 5% aqueous solution of sodium bicarbonate. The organic extract was washed with a saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo, and the crude product was purified by chromatography on silica gel.

5-*endo*-Chloro-2-*endo*-methyl-6-*exo*-phenylselenenyl-7-oxabicyclo[2.2.1]heptan-2-*exo*-ol (8). From 126 mg (1 mmol) of 6 was obtained after 5 min, 238 mg of 8 as a yellow oil (75 %), after chromatography (hexane : ethyl acetate, 2:1, Rf= 0.28). ^{1}H NMR: 1.26 (3H, s, Me), 1.69 (1H, ddtap, J= 14.0, 5.9, 1.2 Hz, H-3x), 2.31 (1H, d, J= 14.0 Hz, H-3n), 2.81 (1H, s, OH), 3.28 (1H, d, J= 4.1 Hz, H-6), 4.01 (1H, ddd, J= 5.1, 4.1, 1.5, Hz, H-5), 4.06 (1H, s, H-1), 4.48 (1H, tap, J= 5.5 Hz, H-4), 7.20-7.24 (3H, m, Ar.), 7.48-7.52 (2H, m, Ar.). ^{13}C NMR: 20.6, 41.2, 46.6, 62.1, 78.2, 80.2, 92.5, 127.9, 128.6 129.1 134.1. IR ($CDCl_3$): 1100, 1220, 1470, 2920-3050, 3400-3500. Anal. Calcd. for $C_{13}H_{15}O_2ClSe$: C, 49.10; H, 4.75; Cl, 11.15. Found: C, 49.16; H, 4.70; Cl, 11.11.

5-*endo*-Chloro-2-*endo*-methyl-6-*exo*-phenylsulfenyl-7-oxabicyclo[2.2.1]heptan-2-*exo*-ol (9). From 126 mg of 6 was obtained after 5 min., 210 mg of 9 as a yellow oil(78%), after chromatography (hexane : ethyl acetate, 3:1, Rf= 0.14). ^{1}H NMR: 1.30 (3H, s, Me), 1.73 (1H, ddtap, J= 14.0, 6.0, 1.3 Hz, H-3x), 2.32 (1H, d, J= 14.0 Hz, H-3n), 2.76 (1H, brs, OH), 3.32 (1H, d, J= 4.0 Hz, H-6), 3.90 (1H, ddd, J= 5.1, 3.7, 1.5 Hz, H-5), 3.98 (1H, s, H-1), 4.52 (1H, tap, J= 5.4 Hz, H-4) 7.15-7.27 (3H, m, Ar.), 7.32-7.36 (2H, m, Ar.). ^{13}C NMR: 20.7, 41.3, 53.4, 61.6, 77.9, 80.1, 91.7, 127.3, 129.0,

131.2, 134.0. IR ($CDCl_3$): 1100, 1220, 1470, 2920-3050, 3400-3500.

5-*endo*-Chloro-2-*exo*-methyl-6-*exo*-phenylselenenyl-7-oxabicyclo[2.2.1]heptan-2-*endo*-ol (12) and 5-*exo*-methyl-2-*exo*-phenylselenenyl-4,7-dioxatricyclo [3.2.1.$0^{3,6}$]octane (13). From 126 mg (1 mmol) of 7 was obtained after 5 min , a 4:1 mixture of 12 and 13. 12 was isolated from the mixture as a yellow oil (65%), after chromatography (chloroform : ethyl acetate, 19:1, Rf= 0.29).**Data of 12:** ^{1}H NMR: 1.40 (3H, s, Me), 1.73 (1H, ddd, J= 13.2, 5.7, 1.4 Hz, H-3x), 1.87 (1H, s, OH), 2.27 (1H, d, J= 13.2 Hz, H-3n); 4.04 (1H, s, H-1), 4.11 (1H, d, J= 4.2 Hz, H-6), 4.22 (1H, ddd, J= 5.7, 4.3, 1.4 Hz, H-5), 4.50 (1H, tap, J= 5.4 Hz, H-4), 7.06-7-57 (5H, m, Ar.). ^{13}C NMR: 29.1, 38.4, 45.1, 63.1, 77.5, 81.6, 90.6, 127.3, 128.8, 128.9, 133.3. IR ($CHCl_3$): 1000, 1210, 1440, 1475, 2850-3050, 3400-3500. Anal. Calcd. for $C_{13}H_{15}O_2ClSe$: C, 49.10; H, 4.75; Cl, 11.15. Found: C, 49.04; H, 4.77; Cl, 11.19. **Data of 13** (From the crude): ^{1}H NMR: 1.41 (3H, s, Me), 1.66 (1H, dd, J= 12.6, 4,6 Hz, H-3x), 2.08 (1H, d, J= 12.6 Hz, H-3n), 3.66 (1H, s, H-5), 4.76 (1H, dd, J= 3.5, 1.6 Hz, H-6), 4.99 (1H, dt, J= 4.5, 1.3 Hz, H-4), 5.09 (1H, d, J= 3.5 Hz, H-1), 7.23-7-29 (3H, m, Ar.), 7.51-7.59 (2H, m, Ar.). ^{13}C NMR: 21.1, 44.4, 49.0, 81.5, 82.2, 84.9, 91.9, 127.5, 128.6, 129.2, 133.7.

5-*exo*-Methyl-2-*exo*-phenylsulfenyl-4,7-dioxatricyclo[3.2.1.$0^{3,6}$]octane (10) and 5-*endo*-chloro-2-*exo*-methyl-6-*exo*-phenylsulfenyl-7-oxabicyclo[2.2.1] heptan-2-*endo*-ol (11). From 126 mg (1 mmol) of 7 was obtained after 5 min a 4:1 mixture of 10 and 11. 10 was isolated from the mixture as a white solid (75%), after chromatography (hexane : ethyl acetate, 5:1, Rf= 0.29).**Data of 10:** mp (hexane : diethyl ether): 93-94°C. ^{1}H NMR: 1.41 (3H, s, Me), 1.64 (1H, dd, J= 12.6, 4.6 Hz, H-3-x), 2.05 (1H, d, J= 12.6 Hz, H-3n), 3.65 (1H, s, H-5), 4.61 (1H, dd, J= 3.5, 1.7 Hz, H-6), 4.91 (1H, dt, J= 4.6, 1.5 Hz, H-4), 5.07 (1H, dd, J= 3.5, 0.9 Hz, H-1), 7.00-7.57 (5H, m, Ar.). NOE: between H-5 (3.65 ppm) / H-Ar: 3.6 %, H-5 / H-3n: 2.9 %, H-5 / H-4: 2.1 %, H-5 / H-6: 1.8 %. ^{13}C NMR: 20.8, 43.6, 53.1, 81.1 (2C), 83.9, 92.0, 126.6, 128.9, 130.3, 133.9. IR (KBr): 740, 880, 960, 980, 1040, 1440, 1480, 2900, 2950, 3050. Anal. Calcd. for $C_{13}H_{14}O_2S$: C, 66.64; H, 6.02; S, 13.68. Found: C, 66.66; H, 6.05; S, 13.62. **Data of 11** (From the crude): ^{1}H NMR: 1.39 (3H, s, Me), 1.73 (1H, ddd, J= 13.2, 5.9, 1.4 Hz, H-3x), 1.88 (1H, br s, OH), 2.26 (1H, d, J= 13.2 Hz, H-3n), 3.94 (1H, s, H-1), 4.08 (1H, ddd, J= 5.1, 4.3, 1.2 Hz, H-5), 4.17 (1H, d, J= 4.3 Hz, H-6), 4.51 (1H, td, J= 5.7, 0.8 Hz, H-4), 7.18-7.78 (5H, m, Ar.). ^{13}C NMR: 29.5, 39.1, 51.3, 62.6, 81.8, 84.9, 90.1, 126.8, 129.1, 130.2, 132.3.

5-*endo*-Chloro-2-*exo*-methyl-7-oxabicyclo[2.2.1]heptan-2-*endo*-ol (14). To a solution of 128 mg (0.40 mmol) of 12 in dry toluene (10 ml / mmol), was added 116.4 mg (0.10 ml, 0.41 mmol) of tributyltin hydride. The mixture was heated at 80°C. A solution of 6.3 mg of AIBN [2,2'-azobis (2-methylpropanenitrile)] in 1 ml of toluene was then added, and the reflux was continued for 3h after which time the solvent was removed in vacuo. The crude was purified by chromatography on silica gel (hexane:ethyl acetate, 3:1, Rf= 0.21). It was obtained 42 mg of 14 (65 %) as a yellow oil. ^{1}H NMR: 1.43 (3H, s, Me), 1.57-1.84 (3H, m), 2.25-2.36 (2H, m),, 4.03 (1H, d, J= 4.9 Hz, H-1), 4.16-4.26(1H, m, H-5x), 4.48 (1H, tap, J= 5.3 Hz, H-4). ^{13}C NMR: 29.3, 33.1, 39.8, 55.3, 77.4, 80.8, 84.9. IR (film): 700, 780, 970, 1220, 2820-2950, 3440.

(1R*,2R*,4R*,)-3',3'-Dichloro-4'-oxa-2,2'-spiro-oxetan-5-*endo*-chloro-6-*exo*-phenylselenenyl-7-oxabicyclo[2.2.1]heptane (19). From 375 mg (1.7 mmol) of 15 was obtained after 4 h, 491 mg of 18 as a white solid (70%), after chromatography (hexane : ethyl acetate, 5:1, Rf= 0.40). mp: 83-85°C, ^{1}H NMR: 2.68 (1H, d, J= 15.3 Hz H-3n), 2.77 (1H, dd, J= 15.3, 5.1 Hz, H-3x), 3.70 (1H, d, J= 4.2 Hz, H-6), 4.27 (1H, t, J= 4.7 Hz, H-5), 4.76 (1H, t, J= 5.1 Hz, H-4), 4.93 (1H, s, H-1), 7.20-7.40 (3H, m, Ar.), 7.45-7.55 (2H, m, Ar.). ^{13}C NMR: 32.9, 44.6, 61.3, 81.6, 85.3, 93.4, 127.5, 129.4, 128.4, 134.1, 155.9. IR (KBr): 760, 1220, 1860, 3020.Anal. Calcd. for $C_{14}H_{11}O_3Cl_3Se$:

C, 40.76; H, 2.69; Cl, 25.78. Found: C, 40.72; H, 2.70; Cl, 25.73.

(1R*,2R*,4R*,)-3',3'-Dichloro-4'-oxa-2,2'-spiro-oxetan-5-*endo*-chloro-6-*exo*-phenylsulfenyl-7-oxabicyclo[2.2.1]heptane (20). From 375 mg (1.7 mmol) of 15 was obtained after 4 h, 391 mg of 20 as a yellow oil (63%), after chromatography (hexane : ethyl acetate, 5:1, Rf= 0.40). ^{1}H NMR: 2.66 (1H, dd, J= 15.3, 1.0 Hz, H-3n), 2.78 (1H, ddd, J= 15.3, 5.2, 0.7 Hz H-3x), 3.75 (1H, d, J= 4.2 Hz, H-6), 4.15 (1H, ddd, J= 4.9, 4.1, 0.9 Hz, H-5), 4.76 (1H, tap, J= 4.8 Hz, H-4), 4.85 (1H, s, H-1), 7.20-7.90 (5H, m, Ar.). ^{13}C NMR: 33.2 52.1, 60.8, 81.4, 84.8, 93.1, 126.8, 129.3, 131.0, 132.9, 159.9. IR (film): 800, 1210, 1060, 1870, 2980-3040.

(1R*,2S*,4R*,)-4'-Oxa-2,2'-spiro-oxetan-5-*endo*-chloro-6-*exo*-phenylselenenyl-7-oxabicyclo[2.2.1]heptane (21). From 237 mg (1.56 mmol) of 16 was obtained after 72 h, 332 mg of 21 as a yellow solid, (62%) after chromatography (hexane : ethyl acetate, 2:1, Rf= 0.30). mp: 90-92°. ^{1}H NMR: 2.20 (1H, dd, J= 14.4, 5.6 Hz, H-3x), 2.83 (1H, d, J= 14.4 Hz, H-3n), 3.38 (1H, d, J= 16.7 Hz, H-3'), 3.56 (1H, d, J= 16.7 Hz, H-3'), 3.78 (1H, d, J= 4.4 Hz, H-6), 4.24 (1H, ddd, J= 5.3, 4.0, 1.2 Hz, H-5), 4.43 (1H, s, H-1), 4.68 (1H, t, J= 5.3 Hz, H-4), 7.31-7.34 (3H, m, Ar.), 7.57-7.59 (2H, m, Ar.). ^{13}C NMR: 34.6, 45.0, 49.5, 61.2, 80.3, 82.0, 87.7, 128.1, 129.3, 133.8, 165.7. IR (KBr): 800, 1020, 1260, 1840, 2950, 3040. Anal. Calcd. for $C_{14}H_{13}O_3ClSe$: C, 48.89; H, 3.81; Cl, 10.31. Found: C, 48.86; H, 3.85; Cl, 10.37.

(1R*,2S*,4R*)-4'-Oxa-2,2'-spiro-oxetan-5-*endo*-chloro-6-*exo*-phenylsulfenyl-7-oxabicyclo[2.2.1]heptane (22). From 237 mg (1.56 mmol) of 16 was obtained after 48 h, 254 mg of 22 as a yellow solid, (55%) after chromatography (hexane : ethyl acetate, 5:1, Rf= 0.20). mp: 74-76°C. ^{1}H NMR: 2.24 (1H, ddd, J= 14.5, 5.5, 1.2 Hz, H-3x), 2.86 (1H, d, J= 14.5 Hz, H-3n), 3.41 (1H, d, J= 16.7 Hz, H-3'), 3.59 (1H, d, J= 16.7 Hz, H-3'), 3.84 (1H, d, J= 4.4 Hz, H-6), 4.12 (1H, ddd, J= 5.4, 3.9, 1.4 Hz, H-5), 4.35 (1H, s, H-1), 4.73 (1H, t, J= 5.4 Hz, H-4), 7.26-7.43 (5H, m, Ar.). ^{13}C NMR: 34.9, 49.6, 52.0, 61.1, 79.9, 81.9, 87.0127.4, 129.3, 130.7, 133.4, 165.5. IR (KBr): 740, 840, 1000, 1130, 1820, 2840-3040. Anal. Calcd. for $C_{14}H_{13}O_3ClS$: C, 56.62; H, 4.41; Cl, 11.94. Found: C, 56.79; H, 4.45; Cl, 11.88.

(1R*,2S*,4R*)-4'-Oxa-2,2'-spiro-oxetan-5-*endo*-bromo-6-*exo*-phenylselenenyl-7-oxabicyclo[2.2.1]heptane (23). From 120 mg (0.78 mmol) of 16 was obtained after 50 h, 236 mg of 23 as a yellow solid (78%), after chromatography (hexane : ethyl acetate, 1:1, Rf= 0.28). mp: 98-100°. ^{1}H-NMR: 2.24 (1H, ddd, J= 14.4, 5.7, 1.5 Hz, H-3x), 2.90 (1H, d, J= 14.4 Hz, H-3n), 3.28 (1H, d, J= 16.7 Hz, H-3'), 3.55 (1H, d, J= 16.7 Hz, H-3') 3.83 (1H, d, J= 4.7 Hz, J= 4.7 Hz, H-6), 4.16, (1H, ddd, J= 5.5, 4.7, 1.5 Hz, H-5), 4.41 (1H, s, H-1), 4.66 (1H, t, J= 5.2 Hz, H-4), 7.30-7.34 (3H, m, Ar.), 7.57-7.60 (2H, m, Ar.). ^{13}C NMR: 36.1, 45.0, 49.3, 51.0, 80.2, 82.1, 87.5, 127.8, 128.8, 129.2, 133.9, 165.5. IR (KBr): 800, 1020, 1130, 1260, 1840, 2950. Anal. Calcd. for $C_{14}H_{13}O_3BrSe$: C, 43.34; H, 3.38; Br, 20.59. Found: C, 43.31; H, 3.43; Br, 20.55.

5-*endo*-Chloro-2-*exo*-2'-hydroxyethyl-6-*exo*-phenylselenenyl-7-oxabicyclo[2.2.1]heptan-2-*endo*-ol (24) and 5-*exo*-2'-hydroxyethyl-2-*exo*-phenyl-selenenyl-4,7-dioxatricyclo[3.2.1.0^{3,6}]octane (25). From 75 mg (0.48 mmol) of 17 was obtained after 5 min, a 5:1 mixture of 24 and 25. These adducts were separated by chromatography (hexane : ethyl acetate, 1:1, **24**: 62%, Rf= 0.28, **25**: 12%, Rf= 0.14). **Data of 24:** ^{1}H NMR: 1.75 (1H, ddd, J= 13.2, 5.6, 1.0 Hz, H-3x), 1.81-1.87 (2H, m, 2H-1'), 2.20 (1H, d, J= 13.2 Hz, H-3n), 2.80 (2H, brs, 2-OH), 3.84-3.88 (2H, m, 2H-2'), 4.12 (1H, s, H-1), 4.13 (1H, d, J= 4.4 Hz, H-6), 4.17 (1H, ddd, J= 5.8, 4.4, 1.3 Hz, H-5), 4.45 (1H, tap, J= 5.2 Hz, H-4), 7.19-7.24 (3H, m, Ar.), 7.50-7.53 (2H, m, Ar.). ^{13}C NMR: 37.2, 40.2, 44.7, 59.4, 63.3, 80.7, 81.6, 89.2, 127.3, 129.0, 133.1. IR (film): 810, 1000-1100, 1260, 1440, 1580, 2480-3050, 3400. **Data of 25:** ^{1}H NMR: 1.65 (1H, dd, J= 12.7, 4.6 Hz, H-3x), 1.76-1.95 (2H, m, 2H-1'), 2.09 (1H, d, J=

12.7 Hz, H-3n), 3.63 (1H, s, H-5), 3.68-3.85 (2H, m, 2H-2'), 3.68- 3.85 (2H, m, 2H-2'), 4.74 (1H, dd, J= 3.5, 1.6 Hz, H-6), 4.97 (1H, dt, J= 4.6, 1.5, Hz, H-4), 5.29 (1H, dd, J= 3.5, 0.5 Hz, H-1), 7.19-7.24 (3H, m, Ar.), 7.45-7.50 (2H, m, Ar.). ^{13}C NMR: 29.7, 36.4, 43.5, 59.6, 80.1, 81.9, 85.9, 95.2, 127.7, 129.3, 133.8. IR (film): 1040, 1480, 2920, 3050, 3400.

5,6-*exo*-Epoxy-2-*exo*-phenyl-7-oxabicyclo[2.2.1]heptan-2-*endo*-ol (31). To a solution of 1 equivalent of 17 in chloroform (10 ml / mmol) at 0°C was added 1.3 equivalent of mCPBA in chloroform (3ml /mmol). The mixture was stirred for 3 h after which time it was quenched with a saturated solution of sodium bicarbonate. The organic extract was washed with a saturated solution of sodium chloride and dried over magnesium sulfate. The solvent was removed in vacuo and the crude product was purified by recrystallization from hexane : chloroform. Pure 31 was obtained as a white solid (92%). (Rf= 0.24, hexane : ethyl acetate, 1:1), mp: 136-138°C. ^{1}H NMR: 1.73 (1H, d, J= 12.9 Hz, H-3n), 2.24 (1H, dd, J= 12.9, 5.3 Hz, H-3x), 2.75 (1H, brs, OH), 3.44 (1H, d, J= 3.4 Hz, H-5 or H-6), 3.72 (1H, d, J= 3.4 Hz, H-5 or H-6), 4.15 (1H, s, H-1), 4.41 (1H, d, J= 5.2 Hz, H-4), 7.16-7.18 (3H, m, Ar.), 7.41-7.44 (2H, m, Ar.). ^{13}C NMR: 45.3, 49.1, 50.0, 75.0, 80.0, 82.8, 124.6, 127.2, 128.2, 146.8. IR (KBr): 850, 1100, 2840-3050, 3480. Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.58; H, 5.92. Found: C, 70.55, H, 5.97.

5-*exo*-Phenyl-4,7-dioxatricyclo[3.2.1.0^{3,6}]octan-2-*exo*-ol (32). To a solution of 1 equivalent of 31 in dry THF (10 ml / mmol) was added 1.3 equivalent of *t*-BuOK. The mixture was stirred at 0°C for 15 min after which time ethyl acetate was added (15 ml / mmol) and the organic extract was washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the crude product was purified by chromatography (ethyl acetate, Rf= 0.40). It was obtained 32 as a white solid (78 %). mp: 82-83°C. ^{1}H NMR: 2.10 (1H, dd, J= 13.1, 4.7 Hz, H-3x), 2.24 (1H,d, J= 13.1 Hz, H-3n), 2.68 (1H, brs, OH), 4.17 (1H, s, H-5), 4.58 (1H, dd, J= 3.3, 1.8 Hz, H-6), 4.98 (1H, d, J= 4.3 Hz, H-4), 5.22 (1H, d, J= 3.4 Hz, H-1), 7.25-7.41 (5H, m, Ar.). ^{13}C NMR: 42.2, 73.7, 82.0, 82.7, 83.5, 93.8, 124.1, 127.6, 128.2, 139.2. IR (KBr): 700, 920, 1050-1100, 2900-3020, 3420. Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.58; H, 5.92. Found: C, 70.64; H, 5.89.

5-*endo*-Chloro-2-*exo*-methyl-6-*exo*-phenylsulfonyl-7-oxabicyclo[2.2.1]heptan-2-*endo*-ol (33) and 2-*exo*-phenylsulfonyl-5-*exo*-methyl-4,7-dioxatricyclo [3.2.1.0^{3,6}]octane (34). To a suspension of 20 equivalents (1.269 g) of potasium carbonate and 128 mg of a 4:1 mixture of 10 and 11 in methylene chloride was added 2 equivalents (190 mg) of mCPBA. The mixture was stirred at 0°C for 12 h after which time it was quenched with saturated solution of sodium bicarbonate and the organic extract was washed with brine. The solution was dried over anhydrous magnesium sulfate and the solvent was removed in vacuo. The crude product was purified by fractional recrystallization in chloroform : hexane. **Data of 33** (pure product): mp: 141-142°C. (Rf= 0.3, hexane : ethyl acetate, 1:1). ^{1}H NMR: 1.50 (3H, s, Me), 1.79 (1H, dd, J= 13.2, 5.6 Hz, H-3x), 2.21 (1H, d, J= 13.4 Hz, H-3n), 2.74 (1H, brs, OH), 4.27 (1H, d, J= 5.13 Hz, H-6),4.40 (1H, tap, J= 5.0 Hz, H-5), 4.58 (1H, tap, J= 5.2 Hz, H-4), 4.62 (1H, s, H-1), 7.59-7.74 (3H, m, Ar.), 7.96-7.98 (2H, m, Ar.), ^{13}C NMR: 28.5, 38.2, 55.8, 68.4, 76.89, 81.2, 84.3, 128.3, 129.2, 134.0, 137.4. IR (KBr): 1100, 1290, 1320, 1450, 2980, 3100, 3500. Anal. Calcd.for $C_{13}H_{15}O_4ClS$: C, 51.57; H, 4.99; Cl, 11.71; S,10.59. Found: C, 51.55; H, 4.93; Cl, 11.67; S, 10.55. **Data of 34** (pure product): mp:132-133°C. (Rf= 0.28, hexane :ethyl acetate, 1:1). ^{1}H NMR: 1.41 (3H, s, Me), 1.65 (1H, dd, J= 12.8, 4.7 Hz, H-3x), 1.98 (1H, d, J= 12.8 Hz, H-3n), 3.64 (1H, s, H-5), 5.01 (1H, d, J= 3.6 Hz, H-1), 5.09 (1H, dd, J= 3.5, 1.8 Hz, H-6), 5.37 (1H, ddd, J= 4.7, 1.8, 1.1 Hz, H-4), 7.52-7.67 (3H, m, Ar.), 7.86-7.81 (2H, m, Ar). ^{13}C NMR: 20.5, 43.3, 70.2, 78.0, 81.0, 81.2, 92.7, 128.2, 128.9, 133.7, 138.4. IR (KBr): 1050, 1290, 2920, 3050. Anal. Calcd. for $C_{13}H_{14}O_4S$: C, 58.64; H, 5.30; S, 12.04. Found: C, 58.69; H, 5.27; S, 12.09.

Acknowledgment. This research was supported by the Ministerio de Educación y Ciencia (Grant. No. PB87-0064) and by the C.S.I.C. One of us (A. V.) gratefully acknowledges the U.C.M. for a doctoral fellowship.

References.

(1) For a preliminary communication, see: Arjona, O.; Fernández de la Pradilla, R.; Pérez, R. A. ; Plumet, J.; Viso, A. *Tetrahedron Lett.* **1987**, *28*, 5549-5550.

(2) For a recent review, see: Lipshutz, B. H. *Chem Rev.* **1986**, *86*, 795-819.

(3) For some leading references, see: (a) Das, J.; Vu, T.; Harris, D. N.; Ogletree, M. L. *J. Med. Chem.* **1988**, *31*, 930-935. (b) Wilson, N. L.; Jones, R. L.; Marr, C. G.; Muir, G. *Eur. J. Med. Chem.* **1988**, *23*, 359-364. (c) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 960-961. (d) Jung. M. E.; Street, L. J. *Heterocycles* **1988**, *27*, 45-48. (e) Reymond, J. L.; Vogel, P. *Tetrahedron Lett.* **1988**, *29*, 3695-3698. (f) Murai, A.; Tanimoto, N.; Sakamoto, N.; Masamune, T. *J. Am. Chem. Soc.* **1988**, *110*, 1985-1986. (g) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542-7543. (h) Katagiri, N.; Akatsuka, H.; Haneda, T.; Kaneko, C.; Sera, A. *J. Org Chem.* **1988**, *53*, 5464-5470.

(4) (a) For a short synthesis of L-Daunosamine, see: Warm. A.; Vogel, P. *J.Org. Chem.* **1986**, *51*, 5348-5353. (b) For a synthesis of (+)- and (-)-Methyl Nonactate, see: Warm, A.; Vogel, P. *Helv. Chim. Acta* **1987**, *70*, 690-700. (c) For a synthesis of D- and L-Ribose derivatives, see: Wagner, J.; Vieira, E.; Vogel, P.; *Helv. Chim. Acta* **1988**, *70*, 624-630.(d) For a synthesis of (±)-Castanospermine, Reymond, J-L.; Vogel, P. *Tetrahedron Lett.* **1989**, *30*, 705-706.

(5) (a) Vieira, E.; Vogel, P. *Helv. Chim. Acta* **1982**, *65*, 1700-1706. (b) Moore, J. A.; Partain, E. *J. Org. Chem.* **1983**, *48*, 1105-1106.(c) Brion, F. *Tetrahedron Lett.* **1982**, *23*, 5299-5302. (d) Nugent, W. A.; McKinney, R.J.; Harlow, R. L. *Organometallics* **1984**, *3*, 1315-1318.

(6) (a) Vieira, E.; Vogel, P. *Helv. Chim. Acta* **1983**, *66*, 1865-1871. (b) Black, K. A.; Vogel, P. *Helv. Chim. Acta* **1984**, *67*, 1612-1615. (c) Takayama, H.; Iyobe, A,; Koizumi, T. *J. Chem. Soc. Chem. Commun.* **1986**, 771-772 (d) Saf, R.; Faber, K.; Penn, G,; Griengl, H. *Tetrahedron* **1988**, *44*, 389-392.

(7) Black, K. A.; Vogel, P. *J. Org.Chem* **1986**,*51*, 5341-5348.

(8) (a) Plumet, J.; Escobar, G.; Manzano, C.; Arjona, O.; Carrupt, P.-A.; Vogel, P. *Heterocycles* **1986**, *24*, 1535-1538. (b) Arjona, O.; Fernández de la Pradilla, R.; Manzano, C.; Pérez, S.; Plumet, J. *Tetrahedron Lett.* **1987**, *28*, 5547-5548. (c) Arjona, O.; Mallo, A.; Manzano, C.; Plumet, J.; Galbis, J.; Jaime, C. *J. Chem. Soc. Perkin Trans II* **1988**, 865-868. (d) Arjona, O.; Fernández de la Pradilla, R.; Pérez, S.; Plumet, J. *Tetrahedron* **1988**, *44*, 1235.

(9) This structure was incorrectly considered to account for the unusually deshielded H-5 and H-6, since H-5 would be placed *exo* with respect to the bicyclic moiety; it is well known that *exo* protons in bicyclo[2.2.1] systems are generally deshielded relative to *endo* protons, see: Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon Press, Oxford, **1969**.

(10) Le Drian and Vogel have recently prepared *endo*- and *exo*-5,6-*exo*-epoxy-7-oxabicyclo[2.2.1]heptan-2-ols, and a difference in chemical shift between both stereoisomers of 0.55 ppm was encountered for H-2. See: Le Drian, C.; Vogel, P. *Helv. Chim. Acta*, **1988**, *71*,1399-1405.

(11) For *endo* electrophilic additions to bicyclo[2.2.2]octene derivatives,see:(a) Claret, F.; Carrupt, P.-A.; Vogel, P. *Helv. Chim. Acta* 1987, *70*, 1886-1896 (b) Carrupt, P.-A.; Vogel, P. *Tetrahedron lett.* 1982, *23*, 2563-2566.

(12) Arjona, O.; Fernández de la Pradilla, R.; Mallo, A.; Pérez, S.; Plumet, J.,*J. Org. Chem.*, in press.

(13) Anteunis, M.; Danneels, D. *Org. Magn. Reson.* 1975, *7*, 345

(14) See ref 9, p.81.

(15) Nicolau, K. C.; Seitz, S. P.; Sipio, W. J.; Blount, J. F. *J. Am. Chem. Soc.* 1979, *101*, 3884-3893.
(16) Nicolau, K. C.; Magolda, R. L.; Sipio, W. J.; Barnette, W. E.; Lisenko, Z.; Joullie, M. M. *J. Am. Chem. Soc.* 1980, *102*, 3784-3793.

(17) See: (a) Brown, W. L.; Fallis, A. G. *Tetrahedron Lett.* 1985, *26*, 607-610 (b) Brown, W. L.; Fallis, A. G. *Can. J. Chem.* 1987, *65*, 1828-1832.

(18) See: (a) Tuladhar, S. M.; Fallis, A. G. *Tetrahedron Lett.* 1987, *28*, 523-526 (b) Tuladhar, S. M.; Fallis, A. G. *Can. J. Chem.* 1987, *65*, 1833-1837.

(19) For an alternative phenylsulfenoetherification method, see: Töteberg-Kaulen, S.; Steckhan, E. *Tetrahedron*, 1988, *44*, 4389-4397.

(20) For leading references in norbornanic systems, see: (a) Waddell, T.G. *Tetrahedron Lett.* 1985, *26*, 6277-6280.(b) Holton, R. A.; Kennedy, R. M. *Tetrahedron Lett.*1984, *25*, 4455-4458.

(21) Soloway, S. B.; Vogel, P.; Le Drian, C. H. A.; Powell, J. E., Patent US, Oct. 06, 1986, US916334.

(22) Shibasaki, M.; Nishida, A.; Ikegami, S. *Tetrahedron Lett.* 1980, *21*, 3061-3064.

(23) Saksena, A. K.; Mangiaracina, P.; Brambilla, R.; McPhail, A. T.; Onan, K. D. *Tetrahedron lett.* 1978,1729-1732.

(24) Arjona, O.; Fernández de la Pradilla, R.; García, L.; Mallo, A.; Plumet, J., *J. Chem. Soc., Perkin Trans. II.* in press.

(25) For some recent references on oxetanes see: (a) The total synthesis of the antiviral, antitumor and antibacterial agent oxetanocin, Nishiyama, S.; Yamamura, S; Kato, K.; Takita, T. *Tetrahedron Lett* 1988, *29*, 4743-4746 (b) Larock, R.C.; Stolz-Dunn, S. K. *Tetrahedron Lett.* 1988, *29*, 5069-5072. (c) Chung, W. S.; Turro, N. J.; Srivastava, S.; Li, H.; le Noble, W. J. *J. Am. Chem. Soc.* 1988, *110*, 7882-7883.

(26) Watson, S. C.; Eastham, J. E. *J. Organomet. Chem.* 1967, *9*, 165.

(27) Fieser and Fieser, *Reagents for Organic Synthesis*, Vol. 5, Pag. 523, John Wiley Sons Inc., USA.

(28) The ^{1}H NMR data of dioxatricyclic derivatives are arbitrarily listed as for bicyclic derivatives in the experimental part of this report, in order to facilitate comparison of the data.