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SUBSTITUENT EFFECTS ON THE REGIOSELECTIVITY OF THE BAEYER-VILLIGER OXIDATION OF 7-OXABICYCLO[2.2.1]HEPTAN-2-ONES

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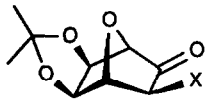
Summary: *New 3-oxy substituted and 3,6-dioxydisubstituted 7-oxabicyclo[2.2.1]heptan-2-ones have been prepared. The regioselectivity of their Baeyer-Villiger oxidation has been determined and compared with that of other 7-oxabicyclo[2.2.1]heptan-2-one derivatives. If the substituent at C(3-*exo*) is an O-acyl or another group less electron-releasing, the bridgehead C(1) migration is favoured, leading to 2,8-dioxabicyclo[3.2.1]octan-3-ones. When the substituent at C(3) is a MeO or (tBu)Me$_2$SiO group, the Baeyer-Villiger oxidation leads to 3,8-dioxabicyclo[3.2.1]octan-2-ones due to preferred C(3) migration. The latter regioselectivity is higher for 3-*endo*-MeO than for 3-*exo*-MeO substituted ketones and it can be enhanced by remote oxy substituents at the C(6-*endo*) position.*

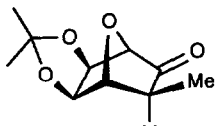
The Baeyer-Villiger oxidation of bicyclic ketones is an important reaction that has been used in synthesis.[1] In many instance and when there are no special steric effects,[2] the regioselectivity of the oxygen atom insertion can be predicted by considering the differential ability of the two concurrent migrating alkyl groups to stabilize a carbenium ion. For example, the Baeyer-Villiger oxidation of the 7-oxabicyclo[2.2.1]-heptan-2-ones **1a-c**, **2** and **3** gives the corresponding urono-6,1-lactones in high yield with less than 5% of



1

a: X=H
b: X=Me
c: X=Br
d: X=OCOAr

Ar=3-Cl-$C_6H_4CO_2$



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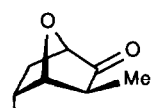

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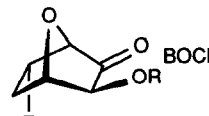
a: Y=H
b: Y=Cl



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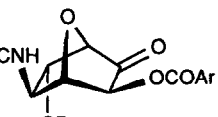
a: Z=Cl, R=ArCO
b: Z=OBn, R=Ac



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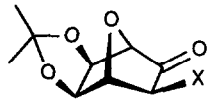
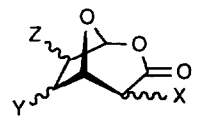


6

a: X=N_3
b: X=NHBOC



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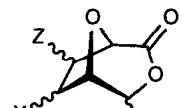
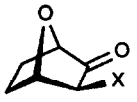


8

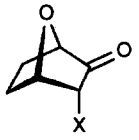
the corresponding isomeric lactones **8**.[3] Interestingly, the 3-acyloxy derivatives **4a,b** and **5** also afford the corresponding furanurono-6,1-lactones **7** in high yield because of a favoured C(1) bridgehead centre migration.[4,5] These results can be interpreted in terms of an ethereal oxygen bridge that is a better electron-releasing substituent at C(1) than the ester substituent at C(3). With the 3-azido and carbamoyl derivatives **6a** and **6b**, respectively, the results were not as straightforward. While **6a** was oxidized into a 45:55 mixture

of the corresponding lactones **7** and **8** with mCPBA (metachloroperbenzoic acid), carbamate **6b** gave exclusively the corresponding 3,8-dioxabicyclo[3.2.1]octan-3-one **8**.[6]

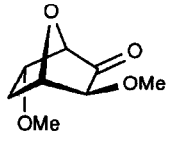
Since the substituted 7-oxabicyclo[2.2.1]heptan-2-ones are powerful synthetic intermediates for the preparation of rare carbohydrates and analogues,[3-7] a reliable model for the substituent effect on the regioselectivity of their Baeyer-Villiger oxidation is most desirable. We have embarked in such a project and wish to report here our preliminary results. We shall be concerned about (a) the effect of exchanging the 3-O-acyl moieties by ethereal groups, (b) the effect of the relative configuration of C(3) (*exo* vs *endo*) and (c) the influence of a polar substituent at the *endo* position of C(6). We thus have prepared the 7-oxabicyclo[2.2.1]heptan-2-ones **9** - **18** and studied their Baeyer-Villiger oxidation.



9 X=H
10 X=OMe
11 X=OBz



12 X=OSiMe$_2$(tBu)
13 X=OMe



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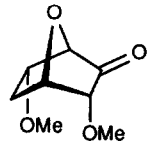

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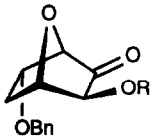
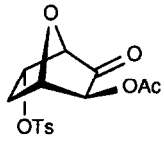


16 R= Bz
17 R= SiMe$_2$(tBu)

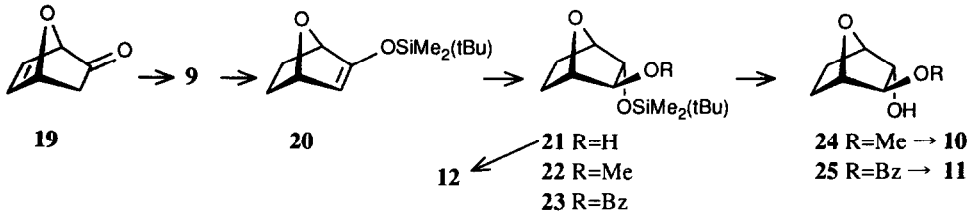


18

Synthesis of the bicyclic ketones.

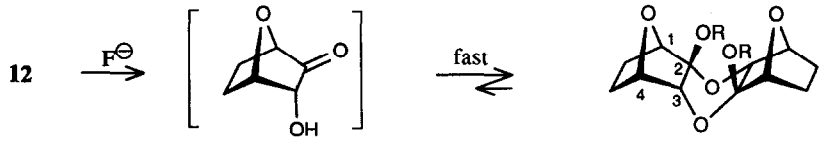
Catalytic hydrogenation (Pd/C, Et_2O) of (±)-7-oxabicyclo[2.2.1]hept-5-en-2-one (**19**)[8] provided **9** (80%). Its silyl enol ether **20** (80%), obtained by treatment first with $(Me_3Si)_2NK$ in THF and then with (tBu)Me$_2$SiCl at -78°C, was hydroborated with BH_3·THF complex and oxidized (H_2O_2/NaOH) into *exo* alcohol **21** (92%). Methylation of **21** (NaH/MeI, THF) led to **22** (75%) which was converted into *endo* alcohol **24** (94%) under usual desilylation conditions (Bu_4NF/H_2O/THF). Oxidation of **24** with pyridinium chlorochromate (PCC) afforded **10** (75%). Benzoylation of *exo* alcohol **21** furnished **23** which was then desilylated into *endo* alcohol **25**. PCC oxidation (CH_2Cl_2, 3 Å molecular sieves) of **25** generated ketone **11** (75%). Under similar conditions, **21** was oxidized to the α-silyloxy ketone **12** (74%).

Scheme 1



Exchange of the tert-butyldimethylsilyl group in **12** by a methyl group could not be achieved simply by cleavage of the silyl ether and methylation of the intermediate alcohol **26** (Scheme 2). When **12** was treated with Bu_4NF in H_2O/THF and then after work-up with NaH and MeI, or with Bu_4NF on silica gel in dry THF and in the presence of MeI, only the dimeric acetal **28** was isolated in 15% yield. This compound resulted form the methylation of diol **27** formed by dimerization of the α-hydroxyketone **26**, even in diluted solutions. Attempts to quench **26** with Ac_2O/pyridine failed to give the corresponding monoacetate and only the dimeric acylal **29** was formed. The structures of **28** - **29** were suggested by their spectral data and by NOE measurements between the signals (δ_H = 3.31 ppm) of the MeO groups and those (δ_H = 4.58 and 3.60 ppm) of the protons at C(1) and C(3) of the bicyclic ether moieties in the ^{1}H-NMR spectrum of **28**. The dimeric hemiacetal **27** results from the addition of the alcoholic moiety of one molecule of **26** onto the *endo* face of the carbonyl group of another molecule of **26** leading finally to a C_2-symmetric system adopting a boat conformation for its 1,4-dioxane moiety.

Scheme 2

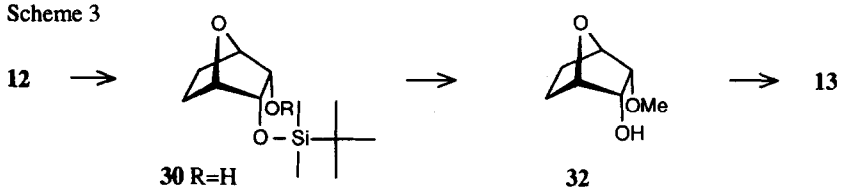


26

27 R=H
28 R=Me
29 R=Ac

For the synthesis of the 3-*endo*-methoxyketone **13** we were forced to develop a rather long procedure as shown in Scheme 3. Reduction of ketone **12** with $NaBH_4$ in MeOH at 0°C gave the *endo* alcohol **30** (92%) whose methylation with NaH/MeI in THF afforded **31** (69%). Desilylation with Bu_4NF/H_2O/THF produced **32** which was oxidized with PCC into **13**.

Scheme 3



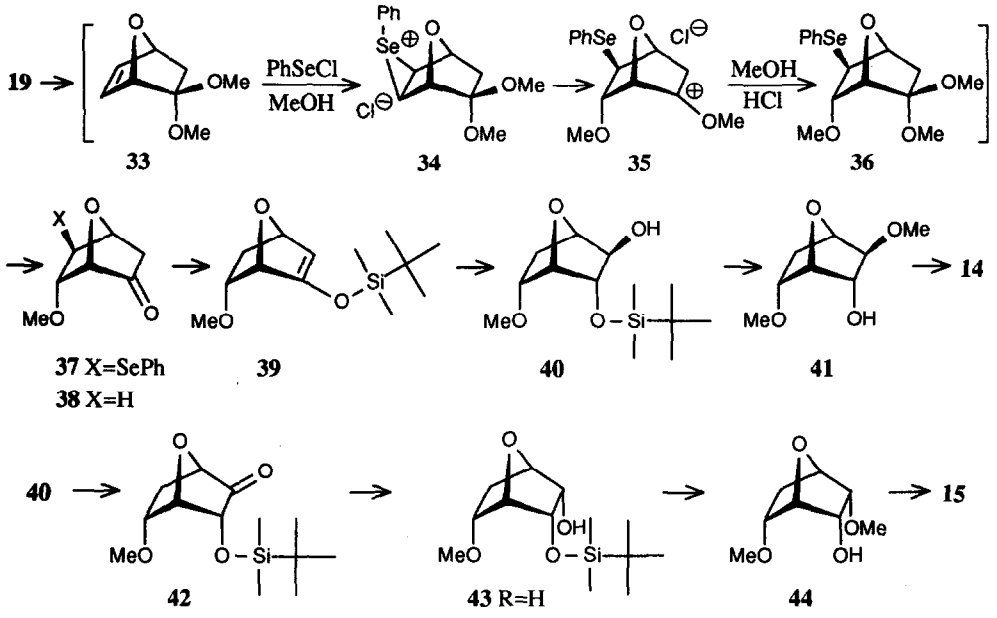
30 R=H
31 R=Me

32

The preparations of the dimethoxyketones **14** and **15** are depicted in Scheme 4. The benzeneselenenyl methoxy adduct **37** was obtained in a "one pot" procedure starting from ketone **19** by treatment with Dowex 50 W in dry MeOH in the presence of $HC(OMe)_3$,[9] followed by addition of benzeneselenyl chloride and then by distillation of methanol and acidic hydrolysis (THF/H_2O/HCl). The overall yield was 73%. This stereoselective addition to the C(5)-C(6) double bond of **33** can be interpreted in terms of the formation of the bridged-ion intermediate **34** which undergoes migration of the *endo* methoxy group from the acetal moiety to centre C(6), leading to the methoxycarbenium intermediate **35** which is quenched by methanol to give **36**[10] which was not isolated but hydrolyzed directly (THF/H_2O/HCl) into ketone **37**. Reductive deselenation of **37** with Bu_3SnH/benzene/AIBN led to **38** (99%), the silyl enol ether **39** of which generated under usual conditions ($(Me_3Si)_2NK$/THF, (tBu)Me_2SiCl, -78°C) was

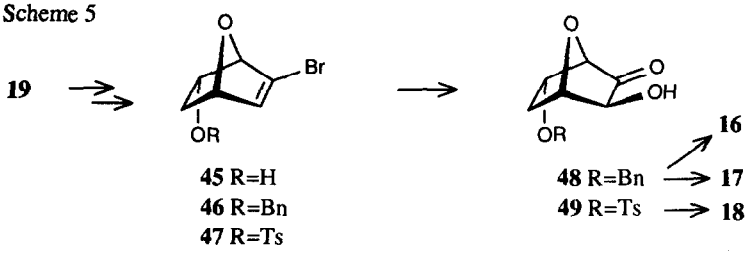
hydroborated with BH_3·THF and oxidized (H_2O_2/NaOH) to produce the *exo* alcohol **40** (35%, based on **38**). Methylation of **40** (NaH, MeI, THF) followed by desilylation (Bu_4NF/H_2O/THF) gave the *endo* alcohol **41** (37%) which was oxidized into ketone **14** (81%) with PCC in CH_2Cl_2 (3 Å molecular sieves). Under the same conditions, the *exo* alcohol **40** was oxidized into **42** which was not isolated and directly reduced with $NaBH_4$/MeOH into **43** (39%). Methylation of the *endo* alcohol **43**, followed by desilylation under standard conditions afforded **44** (23%) which was oxidized into **15** (85%) with PCC.

Scheme 4



The bicyclic ketones **16** - **18** were prepared following the reaction sequence developed in our total synthesis of 3-deoxy-*arabino*-hexose and derivatives[11] (Scheme 5). The *endo* alcohol **45**, derived from the PhSeBr adduct to (±)-7-oxabicyclo[2.2.1]hept-5-en-2-one **19**, was benzylated (BnBr, NaH, Bu_4NI)[12] and tosylated under standard conditions to produce **46** and **47**, respectively. Double hydroxylation with H_2O_2 and a catalytic amount of OsO_4 gave the corresponding α-hydroxyketones **48** and **49**. Benzoylation (Bz_2O, pyr) of **48** gave **16**. Silylation ($tBuMe_2SiCl$, imidazole, DMF) of **48** afforded **17**. Acetylation (Ac_2O/pyr) of **49** furnished **18**. The structures of the new 7-oxabicyclo[2.2.1]heptane derivatives (see Experimental Part) were established by their ^{1}H-NMR spectra[13] and with the help of double irradiation experiments.

Scheme 5



Baeyer-Villiger Oxidations.

The Baeyer-Villiger oxidations of bicyclic ketones **9** - **18** were carried out in $CDCl_3$ with mCPBA (buffered with $NaHCO_3$) and CH_3CO_3H (buffered with CH_3CO_2Na). Our results are shown in the Table. The crude reaction mixtures were analyzed by ^{1}H-NMR once the starting ketone had disappeared (control by TLC on silica gel). The structures of the lactones were deduced from their ^{1}H-NMR spectra and with the help of double irradiation experiments, including NOE measurements. The bridgehead H-C(1) proton is readily recognized by its coupling with H_{exo}-C(7) (^3J = 3-7Hz). The signal of H_{exo}-C(7) is identified unambigously through its couplings with H_{exo}-C(6) and H_{endo}-C(6). The vicinal coupling constant ^3J(H-C(1),H_{endo}-C(7)) is smaller than 1.5 Hz. The bridgehead proton H-C(5) is also recognized by its vicinal couplings with H_{exo}-C(4) (3-4 Hz) and H_{exo}-C(6) (4-7 Hz). Furthermore, when the substituent at C(4) occupies an *exo* position, the coupling constant ^3J(H_{endo}-C(4),H-C(5)) is smaller than 1 Hz.[5,6,11,14] Distinction between lactones of type **7** (furanurono-6,1-lactones if X=OR) resulting from the migration of the bridgehead centre C(1) and of type **8** (2,5-anhydro-hexourono-6,1-lactones if X=OR) resulting from the

Table: Regioselectivities of the Baeyer-Villiger oxidations of bicyclic ketones **9** - **18** in $CDCl_3$.

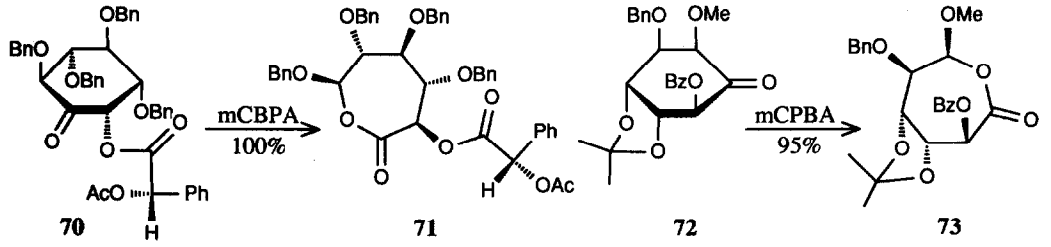
X=H	**9** → **50**	+	**51**	>97:3[a,b]			
X=OMe	**10** → **52**	+	**53**	1:2.8[a] 1:2.6[c] 1:3.8[b] 1:3.6[d]	X=OSiMe$_2$(tBu)	**12** → **56**	+ **57** <3:97[a,b]
X=OBz	**11** → **54**	+	**55**	7.8:1[a] 7.3:1[b]	X=OMe	**13** → **58**	+ **59** <3:97[a,b]
14 →			**60**	+ **61** <3:97[a,b]	**15** →		**62** + **63** <3:97[a,b]
R=Bz	**16** → **64**	+	**65** >95:5				
R=SiMe$_2$(tBu)	**17** → **66**	+	**67** <1:7[a] 1:11[b]			**18** → **68**	+ **69** >95:5

a) with mCPBA/$NaHCO_3$ at 20°C
b) with CH_3CO_3H/CH_3CO_2Na at 20°C
c) with mCPBA/$NaHCO_3$ at 0°C
d) with CH_3CO_3H/CH_3CO_2Na at 0°C

migration of centre C(3) relies also on the chemical shift difference between CH(OR)-OC=O (acylal) and CH(OR)-COO groups, the former being more deshielded than the latter. Lactones of type **8** were less stable than lactones of type **7**, the former being decomposed in the presence of water. The proportion of the two types of lactones was determined by ^{1}H-NMR signal integrations and when they were stable enough, they were isolated and purified for complete characterization (see experimental part).

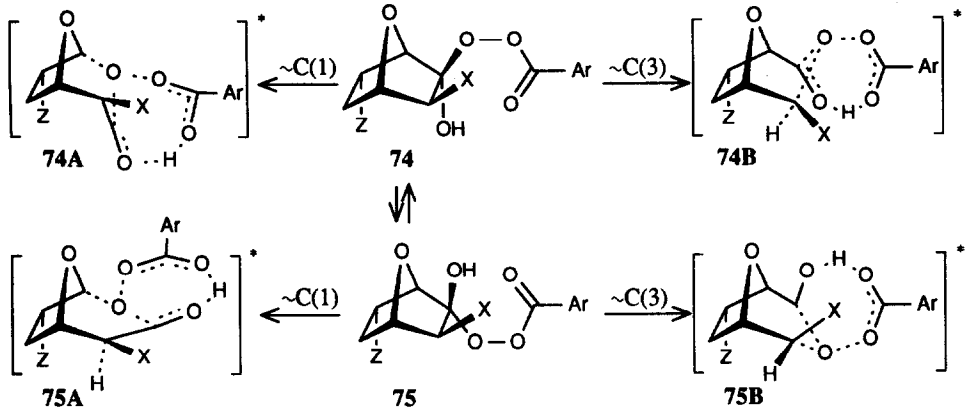
Discussion.

As in earlier cases of Baeyer-Villiger oxidations of 3-O-acyl 3-*exo*-hydroxy-7-oxabicyclo[2.2.1]-heptan-2-one derivatives[2c,d,4,5] our results with esters **11**, **16** and **18** show that the ethereal oxa bridge of this system is a better electron-releasing group than the 3-acyloxy substituent and thus it makes the bridgehead centre C(1) to have a better migratory aptitude than centre C(3). The latter interpretation is supported by the regioselective Baeyer-Villiger oxidations **70** → **71**[15] and **72** → **73**[16] reported by Chida et al. for the oxidation of cyclohexanone derivatives. The major surprise comes with the complete inversion of regioselectivity of the Baeyer-Villiger oxidation when the 3-*exo*-oxy substituent is changed from an ester to a silyl ether moiety. This was indicated with the oxidation of **17** which led to **67** as the major product, the product of C(3) migration. The 3-*exo*-methoxy group also appears to be a stronger migration activator than



the 7-oxa bridge as seen with reaction **10** → **52** + **53**. Interestingly the C(3) centre migratory aptitude is enhanced when the 3-methoxy group is *endo* rather than *exo* (compare **10** → **52** + **53** with **13** → **58** + **59**), or when an *endo* MeO group substitutes centre C(6) of the 3-*exo*-methoxy-ketone as shown with the Baeyer-Villiger oxidation of **14** that led exclusively to **61**, the product of C(3) migration.

Our results with the 3-O-acyl derivatives (X=OCOR) are consistent with the hypothesis[1,2] that favoured bridgehead centre C(1) migrations imply Criegee intermediates of type **74** resulting from the addition of the peracid onto the *exo* face of the bicyclic ketones and that lead to "chair-like" transition state of type **74A**, rather than intermediates of type **75A** (resulting from the *endo* addition of peracid) that would force the transition states **75A** to adopt a "boat-like" conformation. The fact that changing the 3-*exo* substituent from an ester to a silyl ether or methoxy group favours the migration of C(3) centre suggests that either the Criegee intermediates **74** and **75** have similar stabilities and have both the time the be formed in equilibrium with the starting ketones and peracid before the subsequent rearrangements or that the stability difference between "chair-like" and "boat-like" transition states should not be over-emphasized (Pitzer eclipsing interactions in **74A** and **74B** are certainly less important than in cyclohexane analogues; differential anomeric effects might also play a role). At this moment, we cannot rule out the possibility that both transition states of **74A** and **75A** are concurrent in the case of preferred C(1) migrations and that the



transition states **74B** and **75B** also coexist in the case of preferred C(3) migrations. Their relative importance may depends on the nature of the substituent X at C(3) and Z at C(6-*endo*). In such a situation (i.e. no conformational bias or existence of an equilibrium between *exo* and *endo* type of Criegee intermediates **74** ⇄ **75**), the regioselectivity of the Baeyer-Villiger oxidation should be governed by the intrinsic migratory aptitudes of C(1) and C(3), and, therefore, by the differential electron-donating ability of the 7-oxa bridge vs. that of the substituent X at C(3).

It is not clear yet why the MeO group should be a better electron-releasing group than the 7-oxa bridge; moreover, it is not obvious why the directing effect of the 3-*endo*-MeO substituent is better than that of the 3-*exo*-MeO group and why the presence of an 6-*endo*-MeO substituent in **14** suppresses the C(1) centre migration. At this level many hypotheses can be launched such as (1) changes in the rotamer populations of the C(3)-OMe ethers as a function of the relative configuration of C(3) (photoelectron spectra of 3-*exo* and 3-*endo*-methoxybicyclo[2.2.1]heptan-2-one support this hypothesis[17]); the migratory aptitude of the MeOC(3)H group is expected to depend on the orientation of the MeO group as the strongest electron donating effect of that group will operate when its localized n_p nonbonding orbital ($n_1(O)$ - $n_2(O)$ combination) is parallel with the σ(C(3)-C(2)) bond. The MeO group orientation in the transition states of type **74B** and **75B** may differ for *exo*- and *endo*-3-methoxy derivatives and whether an *endo*-6-methoxy is present or not in the bicyclic ketone. (2) According to Noyori et al.,[18] the rotamer population of the C-OH moiety in the Criegee intermediates such **74** and **75** can be affected by remote substituents such MeO group at C(3) or/and at C(6-*endo*); depending on the preferred orientation of the hydroxy group one rearrangement become more facile than the concurrent one. In this hypothesis, the hydroxy group enhances the migratory aptitude of C(1) or C(3) depending on its preferred orientation.

Conclusion.

The regioselectivity of 3-substituted 7-oxabicyclo[2.2.1]heptan-2-ones depends on the electron-releasing ability of the substituent X at C(3). If it is an O-acyl or another group less electron-donating, the 7-oxa bridge dominates the situation and leads to 2,8-dioxabicyclo[3.2.1]octan-3-ones due to preferred C(1) migration. When the substituent at C(3) is a MeO or (tBu)Me_2SiO group, the migratory aptitude of C(3) is

greatly enhanced and the Baeyer-Villiger oxidation leads to the favoured formation of 3,8-dioxabicyclo-[3.2.1]octan-2-ones. The latter regioselectivity can be quite high; it depends on the relative configuration of C(3) (*exo* vs *endo* MeO group) and it can be enhanced by remote substituents at position C(6-*endo*). Much more work is required if a general model of the observed effect should be constructed. Several new, polysubstituted 7-oxabicyclo[2.2.1]heptan-2-one derivatives have been prepared in this work. Systems such as **14** - **19** are in fact anhydro-quercitol analogues.[19] Their Baeyer-Villiger oxidation has generated 3-deoxy-hexofuranurono-6,1-lactone and 2,5-anhydro-3-deoxy-hexourono-6,1-lactone derivatives. These compounds can be obtained, in principle, optically pure in both their D- or L-configuration as the starting 7-oxabicyclo[2.2.1]hept-5-en-2-one is readily available in both its enantiomeric forms ("naked sugar").[20]

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Experimental Part.

General remarks, see ref. 3b.

(±)-2-[(t-Butyl)dimethylsilyloxy]-7-oxabicyclo[2.2.1]hept-2-ene (**20**). Hexamethyldisilazane (HMDS, 12 mL, 57 mmol) was added dropwise to a stirred suspension of KH (2.14 g, 53.3 mmol) in dry THF (20 mL) under Ar atm. The mixture was stirred at 20°C until the production of H_2 ceased. Then it was cooled to -78°C and a solution of **9**[3f] (2.00 g, 17.8 mmol) and (tBu)Me_2SiCl (5.54 g, 97% purity, 35.6 mmol) in dry THF (20 mL) was added dropwise. After 1 h the mixture was added carefully to a sat. aq. soln. of NH_4Cl (100 mL) and Et_2O (200 mL). The two phases were separated and the aq. layer was extracted with Et_2O (200 mL). The combined ethereal layers were washed with H_2O (100 mL) and brine (100 mL), and dried ($MgSO_4$). Distillation of the solvent under atm. pressure with 10 cm Vigreux column left a yellow oil which was distilled at reduced pressure (17 Torr). The fraction distilling over 100°C gave 3.16 g (78%), colourless oil. IR (CH_2Cl_2) ν: 2950, 2930, 2880, 2860, 1620, 1470, 1050 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.91 (m, H-C(4), H-C(3)); 4.53 (d, H-C(1), J = 4.5 Hz); 1.82 (m, H_{exo}-C(5), H_{exo}-C(6)); 1.38 (m, H_{endo}-C(5), H_{endo}-C(6)); 0.94 (s, t-Bu); 0.19, 0.14 (2s, Me_2Si). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 161.4 (s); 103.8 (d, ^1J(C,H) = 170 Hz); 78.9, 78.6 (2d, ^1J(C,H) = 165 Hz); 27.4 (t, ^1J(C,H) = 135 Hz); 25.5 (q, ^1J(C,H) = 125 Hz); 23.6 (t, ^1J(C,H) = 125 Hz); 18.1 (s); 0.9, 0.6 (2q, ^1J(C,H) = 120 Hz). MS (CI, CH_4) m/z: 228 (M^+ +2, 28), 227 (M^+ +1, 87), 226 (M^+, 4), 212 (4), 211 (25), 200 (5), 199 (17), 198 (100), 183 (3), 170 (5), 169 (32), 151 (9), 143 (8), 142 (46), 141 (33), 75 (19). (Found: M^+-C_4H_9, 169.0683. $C_{12}H_{22}O_2Si$-C_4H_9 requires 169.0685).

(1RS,2RS,3RS,4SR)-3-*endo*-[(t-Butyl)dimethylsilyloxy]-7-oxabicyclo[2.2.1]heptan-2-*exo*-ol (**21**). A solution of **20** (2.052 g, 9.064 mmol) in dry THF (20 mL) was cooled in an ice-bath under Ar atm. A solution of borane in THF (10.7 M, 10 mL, 7.0 mmol) was added dropwise with stirring, then the cooling bath was taken away. At the complete disappearance of the starting material (TLC control, silica gel, light petroleum/EtOAc 8:2), 3 N NaOH (2 mL) and then 30% H_2O_2 (2 mL) were added dropwise. The resulting two phase system was stirred for 30 min at 40°C, then it was diluted with Et_2O (100 mL) and H_2O (50 mL). The two phases were separated and the aq. one was extracted with Et_2O (50 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), filtered and concentrated under atm. pressure with a 10 cm Vigreux column to obtain a colourless oil (2.478 g). Flash chromatographic purification (silica gel, light petroleum/EtOAc 4:1) afforded 2.046 g (92%), colourless oil. IR (CH_2Cl_2) ν: 3600 (br.), 3040, 2950, 2930, 2860, 1130, 1115, 865, 845 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.38 (t, H-C(4), J = 5.0 Hz); 4.26 (d, H-C(1), J = 6.0 Hz); 3.88 (dd, H-C(3), J = 1.0, 5.0 Hz); 3.41 (d, H-C(2), J = 1.0 Hz); 2.05, 1.72, 1.46 (m, $H_2C(5)$, $H_2C(6)$); 0.89, (s, t-Bu); 0.11, 0.06 (2s, Me_2Si). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 84.1 (d, ^1J(C,H) = 160 Hz); 82.7, 82.2 (2d, ^1J(C,H) = 150 Hz); 78.7 (d, ^1J(C,H) = 155 Hz); 25.7 (q, ^1J(C,H) = 125 Hz); 25.4 (t, ^1J(C,H) = 130 Hz); 21.2 (t, ^1J(C,H) = 135 Hz); 17.9 (s); 0.8, 0.7 (2q, ^1J(C,H) = 120 Hz). MS (CI, NH_3) m/z: 264 (M^+ +20, 7), 263 (M^+ +19, 18), 262 (M^+ +18, 100), 245 (M^+ +1, 3), 187 (4), 186 (11). (Found: M^+-C_4H_9, 187.0824. $C_{12}H_{24}O_3Si$-C_4H_9 requires 187.0790).

(1RS,2RS,3RS,4RS)-2-*endo*-[(t-Butyl)dimethylsilyloxy]-3-*exo*-methoxy-oxabicyclo[2.2.1]heptane(**22**). A solution of **21** (2.046 g, 8.37 mmol) in dry THF (14 mL) was added dropwise to a stirred suspension of NaH

(290 mg, 80% oil suspension, 9.67 mmol) in dry THF (6 mL) under Ar atm. The mixture was stirred until the production of H_2 ceased, then MeI (0.68 mL, 13 mmol) was added. At the end of the reaction (TLC control, silica gel, light petroleum/EtOAc 7:3) the mixture was diluted with Et_2O (180 mL) and H_2O (90 mL). The two phases were separated and the aq. one was washed with Et_2O (80 mL). The combined organic extracts were washed with brine (90 mL) and dried ($MgSO_4$). Distillation of the solvent under atm. pressure with a 10 cm Vigreux column left a colourless oil (2.402 g). Flash chromatographic purification (silica gel, petroleum ether/EtOAc 8:2) and then distillation under reduced pressure (17 mm Hg) gave 1.633 g (75%), colourless oil. IR (film) ν: 2980, 2960, 2930, 2890, 2860, 1460, 1380, 1360, 1250, 1200, 1135, 1110, 1010, 945, 930, 860, 835, 775 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.38 (d, H-C(4), J = 6.0 Hz); 4.34 (dd, H-C(1), J = 5.0, 5.0 Hz); 3.96 (dd, H-C(2), J = 1.5, 5.0 Hz); 3.32 (s, OMe); 3.02 (d, H-C(3), J = 1.5 Hz); 2.02, 1.72, 1.44 (m, H_2C(5), H_2C(6)); 0.89 (s, t-Bu); 0.08, 0.05 (2s, Me_2Si). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 91.0 (d, J = 150 Hz); 80.1 (d, ^1J(C,H) = 125 Hz); 79.7 (d, ^1J(C,H) = 150 Hz); 78.1 (d, ^1J(C,H) = 145 Hz); 56.4 (q, ^1J(C,H) = 140 Hz); 25.8 (t, ^1J(C,H) = 135 Hz); 25.6 (q, ^1J(C,H) = 130 Hz); 21.4 (t, ^1J(C,H) = 135 Hz); 19.5 (s); 0.8, 0.6 (2q, ^1J(C,H) = 145 Hz). MS (CI, NH_3) m/z: 276 (M^+ +18, 100), 260 (M^+ +2, 3), 259 (M^+ +1, 12), 228 (3), 227 (14), 202 (4), 201 (29), 170 (4), 169 (29), 89 (11). (Found: M^+-C_4-H_9, 201.0943. $C_{13}H_{26}O_3Si$-C_4H_9 requires 201.0947).

(1SR,2SR,3RS,4RS)-3-*exo*-Methoxy-7-oxabicyclo[2.2.1]heptan-2-*endo*-ol (**24**). Tetrabutylammonium fluoride·3H_2O (2.40 g, 98%, 7.45 mmol) was added to a solution of **22** (1.91 g, 7.39 mmol) in Et_2O (34 mL) and the mixture was stirred overnight. At the end of the reaction (TLC control, silica gel, petroleum ether/EtOAc 7:3), the whole solution was purified by column chromatography (silica gel, Et_2O). The fractions were concentrated at atm. pressure with a 25 cm Vigreux column, to afford 1.00 g (94%), colourless oil. IR (film) ν: 3400 (br.), 2980, 2950, 2900, 2820, 1460, 1370, 1335, 1280, 1250, 1200, 1135, 1110, 1090, 1060, 1000, 990, 920 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.77-4.42 (m, H-C(2), H-C(1)); 4.07 (d, H-C(4), J = 5.5 Hz); 3.36 (s, MeO); 3.14 (d, H-C(3), J = 1.5 Hz); 2.11-1.96, 1.86-1.69, 1.62-1.39 (m, H_2C(5), H_2C(6)). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 90.6 (d, ^1J(C,H) = 145 Hz); 80.4 (d, ^1J(C,H) = 155 Hz); 79.0 (d, ^1J(C,H) = 150 Hz); 77.9 (d, ^1J(C,H) = 155 Hz); 56.2 (q, ^1J(C,H) = 140 Hz); 25.8 (t, ^1J(C,H) = 135 Hz); 21.3 (t, ^1J(C,H) = 136 Hz). MS (CI, NH_3) m/z: 162 (M^+ +18, 100), 145 (M^+ +1, 14), 144 (M^+, 1), 127 (4), 126 (4), 113 (5), 112 (11), 100 (18), 87 (16), 84 (10). (Found: M^+, 144.0812. $C_7H_{12}O_3$ requires 144.0786).

(1SR,3RS,4RS)-3-*exo*-Methoxy-7-oxabicyclo[2.2.1]heptan-2-one (**10**). A solution of **24** (1.00 g, 6.94 mmol) in dry CH_2Cl_2 (20 mL) was added dropwise to a stirred suspension of pyridinium chlorochromate (PCC, 2.40 g, 11.1 mmol) and 3 Å molecular sieves in dry CH_2Cl_2 (20 mL) under Ar atm. at 20°C. After 5 h, Et_2O (40 mL) was added and stirring was continued for an additional 30 min. Then the mixture was filtered through silica gel, rinsing with Et_2O. Distillation of the solvent at atm. pressure with a 10 cm Vigreux column left 739 mg (75%) of a colourless oil. The purity of this oil was high enough to carry the Baeyer-Villiger reaction. IR (film) ν: 2990, 2960, 2830, 1770, 1460, 1200, 1110, 1095, 1040, 1010, 920, 910, 890 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.33, 4.28 (m, H-C(1), H-C(4)); 3.45 (s, Me); 3.17 (s, H-C(3)); 2.00-1.77, 1.65-1.51 (m, H_2C(5), H_2C(6)). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 208.8 (s); 81.4 (d, ^1J(C,H) = 150 Hz); 79.7 (d, ^1J(C,H) = 165 Hz); 78.0 (d, ^1J(C,H) = 165 Hz); 57.9 (q, ^1J(C,H) = 140 Hz); 24.3, 24.1 (2t, ^1J(C,H) = 140 Hz). MS (70 eV) m/z: 142 (M^+, 0.2), 114 (8), 113 (1), 99 (3), 98 (1), 97 (2), 87 (2), 86 (8), 85 (19), 84 (11), 83 (3), 82 (4), 81 (4), 73 (2), 72 (6), 71 (34), 70 (7), 69 (8), 61 (1), 59 (6), 58 (100), 57 (7), 55 (19), 53 (9). (Found: M^+, 142.0629. $C_7H_{10}O_3$ requires 142.0629).

(1SR,3SR,4RS)-3-*endo*-[(t-Butyl)dimethylsilyloxy]-7-oxabicyclo[2.2.1]heptan-2-one (**12**). A solution of **21** (423 mg, 1.73 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise to a suspension of PCC (592 mg, 2.75 mmol) and 3 Å molecular sieves in dry CH_2Cl_2 (5 mL) under Ar atm. at 20°C. The mixture was stirred overnight, then Et_2O (10 mL) was added and stirring was continued for an additional 30 min. The mixture was filtered through silica gel, washing with Et_2O. Distillation of the solvent at atm. pressure with a 10 cm Vigreux column afforded 309 mg (74%), colourless oil. IR (film) ν: 2955, 2930, 2860, 1770, 1460, 1250, 1190, 1165, 1130, 1080, 1000 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.64 (dd, H-C(4), J = 6.0, 6.0 Hz); 4.41 (d, H-C(1), J = 6.5 Hz); 4.16 (d, H-C(3), J = 6.0 Hz); 2.17-1.65 (m, H_2C(5), H_2C(6)); 0.89 (s, t-Bu); 0.13, 0.07 (2s, Me_2Si). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 210.9 (s); 81.3 (d, ^1J(C,H) = 170 Hz); 79.3 (d, ^1J(C,H) = 160 Hz); 76.3 (d, ^1J(C,H) = 140 Hz); 27.4 (t, ^1J(C,H) = 130 Hz); 25.8 (q, ^1J(C,H) = 120 Hz); 21.6 (t, ^1J(C,H) = 135 Hz); 18.4 (s); -4.6, -5.0 (2q, ^1J(C,H) = 120 Hz). MS (CI, NH_3 m/z: 261 (M^+ +19, 29), 260 (M^+ +18, 100), 243 (M^+ +1, 16), 186 (9), 185 (46), 184 (2), 157 (14), 127 (4).

(1SR,2RS,3SR,4RS)-3-*endo*-Hydroxy-7-oxabicyclo[2.2.1]hept-2-*exo*-yl benzoate (**25**). A solution of benzoyl chloride (0.7 mL, 5.6 mmol) in dry CH_2Cl_2 (4 mL) was added dropwise to a stirred solution of **22** (579 mg, 2.40 mmol) and Et_3N (0.8 mL, 5.7 mmol) in CH_2Cl_2 (8 mL) and the resulting mixture was stirred at 20°C overnight. Then it was diluted with CH_2Cl_2 and washed successively with H_2O, 5% aq. HCl, 5% aq. $NaHCO_3$ and brine, and then dried ($MgSO_4$). Distillation of the solvent under reduced pressure, followed by flash

chromatographic purification (silica gel, light petroleum/EtOAc 9:1) afforded 469 mg (56%), colourless oil. The oil was dissolved in THF (30 mL) and $Bu_4NF{\cdot}3H_2O$ (420 mg, 1.33 mmol) was added. At the end of the reaction (TLC control, silica gel, light petroleum/EtOAc 8:2) the whole solution was filtered over silica gel and the solvent was distilled under reduced pressure, to afford 150 mg (27%), white solid. IR (KBr) ν: 3520 (br.), 2990, 2960, 2880, 1700, 1450, 1365, 1320, 1295, 1275, 1240, 1195, 1180, 1115, 1090, 1070, 1050, 1025, 1010, 990, 950, 930, 770, 715 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 8.02 (m, Ph); 7.55 (m, Ph); 7.43 (m, Ph); 4.62 (d, H-C(1), J = 6.0 Hz); 4.55 (dd, H-C(4), J = 5.5, 5.5 Hz); 4.42 (d, H-C(2), J = 2.0 Hz); 4.12 (d, H-C(3), J = 5.0 Hz); 2.23-1.50 (m, $H_2C(5)$, $H_2C(6)$). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 167.5 (s); 133.2, 129.6 (2d, ^1J(C,H) = 165 Hz); 129.3 (s); 128.3 (d, ^1J(C,H) = 165 Hz); 85.8, 80.8 (2d, ^1J(C,H) = 160 Hz); 80.0, 77.9 (2d, ^1J(C,H) = 150 Hz); 26.5, 21.1 (2t, ^1J(C,H) = 135 Hz). MS (CI, NH_3) m/z: 235 (M^+ +1, 2), 129 (M^+ -(OCPh), 2), 123 (2), 122 (3), 113 (M^+ -(O_2CPh), 6), 112 (M^+ -(HO_2CPh), 43), 106 (8), 105 ($(PhCO)^+$, 100), 77 (Ph^+, 37), 85 (3), 84 (6), 83 (10). (Found: M^+, 234.0879. $C_{13}H_{14}O_4$ requires 234.0892).

(1RS,2RS,4SR)-3-Oxo-7-oxabicyclo[2.2.1]hept-2-*exo*-yl benzoate (**11**). A solution of **25** (151 mg, 0.645 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise to a stirred suspension of PCC (200 mg, 0.928 mmol) in dry CH_2Cl_2 (5 mL) in the presence of 3 Å molecular sieves and stirred overnight. The mixture was then diluted with Et_2O (5 mL) and stirred an additional h. Filtering over silica gel, distillation of the solvents under reduced pressure and flash chromatographic purification (silica gel, light petroleum/EtOAc 7:3) afforded 129 mg (86%), white sirup. IR (film) ν: 3060, 2960 (br.), 2880, 1780, 1720, 1600, 1585, 1490, 1450, 1350, 1315, 1295, 1260 (br.), 1175, 1110, 1070, 1020, 995, 920, 770, 710 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 8.05 (m, Ph); 7.55 (m, Ph); 7.42 (m, Ph); 4.82 (s, H-C(2)); 4.78 (d, H-C(4), J = 5.5 Hz); 4.48 (d, H-C(1), J = 5.5 Hz); 2.13-1.70 (m, $H_2C(5)$, $H_2C(6)$). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 205.9 (s); 165.9 (s); 133.5 (d, ^1J(C,H) = 160 Hz); 129.9 (d, ^1J(C,H) = 165 Hz); 128.8 (s); 128.4 (d, ^1J(C,H) = 160 Hz); 80.3, 78.3 (2d, ^1J(C,H) = 165 Hz); 74.3 (d, ^1J(C,H) = 155 Hz); 24.9, 23.8 (2t, ^1J(C,H) = 135 Hz). MS (CI, NH_3) m/z: 233 (M^+ +1, 18), 123 (2), 122 (3), 110 (4), 106 (25), 105 ($PhCO^+$, 100), 99 (4), 94 (4), 83 (8), 82 (55), 78 (5), 77 (4).

(1RS,2SR,3SR,4SR)-3-*endo*-[(t-Butyl)dimethylsilyloxy]-7-oxabicyclo[2.2.1]heptan-2-*endo*-ol (**30**). $NaBH_4$ (50 mg, 1.3 mmol) was added portionwise to a solution of **12** (322 mg, 1.33 mmol) in methanol (8 mL) cooled to -15°C. At the end of the reaction (TLC control, silica gel, light petroleum/EtOAc 8:2) Et_2O (40 mL) and H_2O (20 mL) were added. The two phases were separated and the ethereal one was washed with H_2O (10 mL) and then with brine (10 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure and 20°C to afford 300 mg (92%), colourless oil. IR (film) ν: 3500 (br.), 2980, 2950, 2930, 2860, 1460, 1385, 1360, 1255, 1180, 1125, 1045, 1020, 1000, 930, 900, 880, 835, 780 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.48 (m, H-C(4)); 4.36 (m, H-C(1)); 3.94 (dd, H-C(3), J = 5.0, 9.0 Hz); 3.81 (m, H-C(2)); 2.05 - 1.85 (m, H_{endo}-C(5), H_{endo}-C(6)); 1.56-1.38 (m, H_{exo}-C(5), H_{exo}-C(6)); 0.90 (s, t-Bu); 0.11, 0.08 (2s, Me_2Si). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 80.2, 79.3 (2d, ^1J(C,H) = 160 Hz); 68.0 (d, ^1J(C,H) = 150 Hz); 66.8 (d, ^1J(C,H) = 155 Hz); 25.7 (q, ^1J(C,H) = 125 Hz); 22.1 (t, ^1J(C,H) = 135 Hz); 21.7 (t, ^1J(C,H) = 135 Hz); 18.0 (s); 1.0, 0.5 (2q, ^1J(C,H) = 120 Hz): MS (CI, NH_3) m/z: 246 (M^+ +2, 18), 245 (M^+ +1, 67), 244 (M^+, 0.5), 187 (17), 171 (5), 170 (19), 169 (76), 159 (14), 143 (11), 131 (6), 95 (20), 92 (20), 76 (11), 75 (100), 74 (25), 73 (33). (Found: M^+-C_4H_9, 187.0815. $C_{12}H_{24}O_3Si$-C_4H_9 requires 187.0790).

(1SR,2SR,3SR,4RS)-2-*endo*-[(t-Butyl)dimethylsilyloxy]-3-*endo*-methoxy-7-oxabicyclo[2.2.1]heptane (**31**). A solution of **30** (3.11 g, 12.7 mmol) in dry THF (10 mL) was added to a stirred suspension of NaH (425 mg, 80% oil suspension, 13.9 mmol), and MeI (1.6 mL, 15 mmol) in dry THF (10 mL) under Ar atm. at 20°C. At the end of the reaction (TLC control, silica gel, light petroleum/EtOAc 9:1) the mixture was diluted with H_2O (100 mL) and Et_2O (150 mL). The two phases were separated and the organic one was washed with brine (100 mL) and dried ($MgSO_4$). Distillation of the solvent under atm. pressure with a 10 cm Vigreux column left an orange oil. Flash chromatographic purification of the oil (silica gel, pentane/Et_2O 95:5) afforded 2.27 g (69%) colourless oil. IR (CH_2Cl_2) ν: 3000, 2960, 2940, 2900, 2860, 1460, 1360, 1200, 1150, 1125, 1105, 1015, 1000, 900, 880, 840 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.50 (dd, H-C81), J = 5.0, 5.0 Hz); 4.34 (dd, H-C(4), J = 5.0, 5.0 Hz); 4.00 (dd, H-C(3), J = 8.5, 5.0 Hz); 3.43 (dd, H-C(2), J = 8.5, 5.0 Hz); 3.32 (s, MeO); 2.17-2.00 (m, H_{endo}-C(5), H_{endo}-C(6)); 1.52-1.43 (m, H_{exo}-C(5), H_{exo}-C(6)); 1.90 (s, t-Bu); 1.08, 1.05 (2s, Me_2Si). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 80.1, 78.8 (2d, ^1J(C,H) = 160 Hz); 77.1, 65.1 (2d, ^1J(C,H) = 150 Hz); 58.1 (q, ^1J(C,H) = 140 Hz); 25.8 (q, ^1J(C,H) = 125 Hz); 22.6, 21.9 (2d, ^1J(C,H) = 135 Hz); 18.2 (s); 0.7, 0.6 (2q, ^1J(C,H) = 120 Hz). MS (CI, NH_3) m/z: 260 (M^+ +2, 18), 259 (M^+ +1, 52), 258 (M^+, 0.31), 203 (3), 202 (11), 201 (67), 173 (3), 171 (7), 170 (14), 169 (100), 89 (40). (Found: M^+-C_4H_9, 201.0961. $C_{13}H_{26}O_3Si$-C_4H_9 requires 201.0947).

(1SR,2SR,3RS,4RS)-3-*endo*-Methoxy-7-oxabicyclo[2.2.1]heptan-2-*endo*-ol (**32**). $Bu_4NF{\cdot}3H_2O$ (2.00 g, 98%, 6.92 mmol) was added to a solution of **31** (1.59 g, 6.15 mmol) in Et_2O (20 mL) and the resulting mixture was stirred at 20°C for 4 days. At the end of the reaction (TLC control, silica gel, light petroleum/EtOAc 8:2), the whole solution was purified by column chromatography (silica gel, Et_2O) and the collected fractions were

concentrated at atm. pressure 25 cm Vigreux column to afford 1.17 g of a colourless oil. The purity of the oil was sufficient to proceed to the next step. IR (film) v: 3450 (br.), 2990, 2940, 2830, 1460, 1200, 1130, 1045, 1010 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.52 (m, H-C(4)); 4.41 (m, H-C(1)), 3.91 (ddd, H-C(2), J = 5.5, 6.0, 9.0 Hz); 3.48 (dd, H-C(3), J = 4.5, 9.0 Hz); 3.36 (s, OMe); 2.88 (d, OH, J = 6.0 Hz); 2.00-1.79 (m, H_{endo}-C(5), H_{endo}-C(6)); 1.55-1.38 (m, H_{exo}-C(5), H_{exo}-C(6)). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 79.8, 78.0 (2d, ^1J(C,H) = 160 Hz); 75.7, 67.3 (2d, ^1J(C,H) = 150 Hz); 58.5 (q, ^1J(C,H) = 140 Hz); 22.2 (t, ^1J(C,H) = 110 Hz); 21.6 (t, ^1J(C,H) = 110 Hz). MS (CI, NH_3)m/z: 162 (M^+ +18, 19), 145 (M^+ +1, 5), 144 (M^+, 6), 127 (11), 126 (15), 115 (3), 113 (11), 112 (59), 111 (8), 101 (11), 100 (87), 99 (29), 98 (14), 97 (24), 95 (13), 94 (18), 88 (11), 87 (100), 85 (28). (Found: M^+, 144.0812. $C_7H_{12}O_3$ requires 144.0786).

(1SR,3RS,4RS)-3-*endo*-Methoxy-7-oxabicyclo[2.2.1]heptan-2-one (**13**). A solution of **32** (1.17 g) in dry CH_2Cl_2 (15 mL) was added dropwise to a stirred suspension of PCC (2.27 g, 10.5 mmol) and 3 Å molecular sieves in dry CH_2Cl_2 (15 mL). At the end of the reaction (TLC control, silica gel, light petroleum/EtOEt 8:2), the mixture was diluted with Et_2O (100 mL), stirred an additional 2 h and filtered through silica gel, washing with Et_2O. Distillation of the solvent under atm. pressure with a 10 cm Vigreux column followed by flash chromatographic purification (silica gel, CH_2Cl_2) afforded 526 mg (60% based on **31**), colourless oil. IR (film) v: 2990, 2950, 2880, 2830, 1765, 1460, 1350, 1280, 1200, 1130, 1080, 1010, 980, 960, 925, 890, 870, 850, 820, 780 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.84 (dd, H-C(4), J = 5.5, 5.5 Hz); 4.42 (d, H-C(1), J = 6.0 Hz); 3.87 (d, H-C(3), J = 5.5 Hz); 3.53 (s, OMe); 2.12-1.90, 1.84-1.67 (m, H_2C(5), H_2C(6)). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 209.3 (s); 82.4 (d, ^1J(C,H) = 150 Hz); 80.5 (d, ^1J(C,H) = 170 Hz); 77.0 (d, ^1J(C,H) = 160 Hz); 58.7 (q, ^1J(C,H) = 140 Hz); 26.6, 21.2 (2t, ^1J(C,H) = 135 Hz). MS (CI, CH_4) m/z: 142 (M^+, 9), 114 (2), 86 (4), 85 (3), 84 (6), 82 (2), 81 (3), 74 (2), 73 (2), 72 (4), 71 (21), 70 (1), 69 (8), 59 (8), 58 (100), 57 (2), 56 (3), 55 (15), 53 (11). (Found: M^+, 142.0634. $C_7H_{10}O_3$ requires 142.0630).

(1RS,4RS,5RS,6RS)-5-*exo*-Benzeneselenyl-6-*endo*-methoxy-7-oxabicyclo[2.2.1]heptan-2-one (**37**). A mixture of (±)-7-oxabicyclo[2.2.1]hept-5-en-2-one[8] (**19**, 6 g, 54.4 mmol), anh. MeOH (60 mL), $CH(OMe)_3$ (60 mL) and DOWEX 50 W acidic resin (1.6 g) was stirred at 20°C overnight. After the addition of MeOH (100 mL) and cooling to 0°C, benzeneselenyl chloride (10.5 g, 55 mmol) in MeOH (200 mL) was added dropwise under vigourous stirring. The resin was filtered off and the solvent was evaporated in vacuo. The crude was dissolved in THF (100 mL) and 5% aq. HCl (25 mL) was stirred overnight at 20°C. The mixture was diluted with 5% Na_2CO_3 (100 mL) and extracted with CH_2Cl_2 (50 mL, 3 times). The combined extracts were dried ($MgSO_4$), the solvent was distilled off, yielding a yellow oil. The oil was crystallized from Et_2O at -20°C to afford 11.84 g (73%), colourless crystals, m.p. 59-60°C. IR (KBr) v: 3070, 3000, 2980, 2940, 2880, 2830, 1760, 1570, 1455, 1435, 1395, 1355, 1310, 1215, 1175, 1150, 1010, 895, 780, 740 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 7.55 (m, C_6H_6); 7.28 (m, C_6H_6); 4.71 (ddd, H-C(4), J = 1.0, 1.0, 6.0 Hz); 4.43 (d, H-C(1), J = 5.5 Hz); 3.95 (dddd, H-C(6), J = 1.0, 1.0, 2.0, 5.5 Hz); 3.31 (d, H-C(5), J = 2.0 Hz); 3.20 (s, OMe); 2.52 (dddd, H_{exo}-C(3), J = 1.0, 1.0, 6.0, 18.0 Hz); 2.14 (d, H_{endo}-C(3), J =18.0 Hz). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 206.7 (s), 134.2 (d, ^1J(C,H) = 160 Hz); 129.4 (d, ^1J(C,H) = 160 Hz); 129.0 (s); 128.1 (d, ^1J(C,H) = 160 Hz); 85.2 (d, ^1J(C,H) = 155 Hz); 81.7 (d, ^1J(C,H) = 165 Hz), 81.4 (d, ^1J(C,H) = 165 Hz); 58.3 (q, ^1J(C,H) = 140 Hz); 48.2 (d, ^1J(C,H) = 150 Hz); 43.4 (t, ^1J(C,H) = 135 Hz). MS (CI, NH_3) m/z: 300 (M^+ (Se^{82}), 7), 298 (M^+ (Se^{80}), 31), 296 (M^+ (Se^{78}), 13), 295 (M^+ (Se^{77}), 6), 294 (M^+ (Se^{76}), 8), 157 (PhSe, 19), 155 (9), 153 (4), 141 (M^+ -PhSe, 27), 117 (12), 115 (12), 109 (14), 85 (18), 81 (86), 77 (26), 71 (100). Anal. calc. for $C_{13}H_{14}O_3Se$ (297.21): C 52.54, H 4.75; found: C 52.60, H 4.79.

(1RS,4SR,6SR)-6-*endo*-Methoxy-7-oxabicyclo[2.2.1]heptan-2-one (**38**). (n-Bu)$_3$SnH (3.6 mL, 98%, 13.3 mmol) was added dropwise to a solution of **37** (2.0 g, 6.73 mmol) in benzene (28 mL) heated under reflux. At the end of the reaction (TLC control, silica gel, light petroleum/EtOAc 7:3) half of the benzene was distilled off under atm. pressure with a 10 cm Vigreux column. The remaining solution was purified by column flash chromatography (silica gel, CH_2Cl_2) to afford 950 mg, colourless oil. IR (film) v: 3010, 2950, 2920, 2840, 1770, 1460, 1410, 1360, 1325, 1285, 1225, 1200, 1150, 1115, 1085, 1020, 1000, 975, 920, 840, 820, 780 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.77 (dd, H-C(4), J = 5.5, 6.0 Hz); 4.31 (d, H-C(1), J = 5.5 Hz); 3.97 (m, H-C(6)); 3.25 (s, OMe); 2.43 (dd, H_{exo}-C(3), J = 6.0, 18.0 Hz); 2.25 (m, H_{exo}-C(5)); 2.05 (d, H_{endo}-C(3), J = 18.0 Hz); 1.49 (dd, H_{endo}-C(5), J = 2.5, 13.0 Hz). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 208.1 (s), 80.6 (d, ^1J(C,H) = 165 Hz); 78.0, 76.0 (2d, ^1J(C,H) = 160 Hz); 57.4 (q, ^1J(C,H) = 145 Hz); 43.3, 35.8 (2t, ^1J(C,H) = 135 Hz). MS (70 eV) m/z: 142 (M^+, 9), 114 (2), 86 (4), 85 (3), 84 (6), 81 (3), 72 (4), 71 (21), 69 (8), 59 (8), 58 (100). (Found: M^+, 142.0615. $C_7H_{10}O_3$ requires 142.0630).

(1RS,2RS,3SR,4SR,5RS)-3-*endo*-t-Butyldimethylsilyloxy-5-*endo*-methoxy-7-oxabicyclo[2.2.1]heptan-2-*exo*-ol (**40**). $(Me_3Si)_2NH$ (3.5 mL, 16 mmol) was added dropwise to a stirred suspension of KH (700 mg, 17.1 mmol) in dry THF (30 mL) under Ar atm. The mixture was stirred at 20°C until the production of H_2 ceased. It was then cooled to -78°C and a solution of **38** (1.60 g, 11.2 mmol) and (t-Bu)Me_2SiCl (2.56 g, 17.0 mmol) in dry THF (30 mL) was added dropwise. The cooling bath was taken away. At the complete disappearance

of starting material (TLC control, silica gel, light petroleum/EtOAc 8:2) a solution of diborane in THF (1.4 M, 8 mL, 11 mmol) was added dropwise and stirring at 20°C was continued until the end of the reaction (TLC control, silica gel, light petroleum/EtOAc 8:2). Then 3 N NaOH (8 mL) and 30% H_2O_2 (10 mL) were added dropwise. The resulting two phase system was stirred for 1 h at 40°C, then it was diluted with Et_2O and H_2O. The two phases were separated and the aq. one was extracted with Et_2O. The combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated under atm. pressure with a 10 cm Vigreux column to afford a colourless oil. Flash chromatographic purification (silica gel, CH_2Cl_2) afforded 1.07 g (35%), colourless oil. IR ($CHCl_3$) ν: 3400 br., 2940, 2920, 2880, 2850, 1630, 1455, 1245, 1220, 830, 770 cm^{-1}.^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.29 (dd, H-C(4), J = 4.5, 4.4 Hz); 4.24 (d, H-C(1), J = 6.5 Hz); 4.13 (m, H-C(3)); 3.96 (ddd, H-C(5), J = 1.5, 4.5, 10.0 Hz); 3.69 (dd, H-C(2), J = 2.0, 8.0 Hz); 3.31 (s, OMe); 2.31 (ddd, H_{exo}-C(6), J = 6.5, 10.0, 12.5 Hz); 1.39 (dd, H_{endo}-C(6), J = 4.4, 12.5 Hz); 0.89 (s, t-Bu); 0.12, 0.09 (2s, Me_2Si). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 85.6 (d, ^1J(C,H) = 145 Hz); 85.2 (d, ^1J(C,H) = 160 Hz); 81.6 (d, ^1J(C,H) = 150 Hz); 76.0 (d, ^1J(C,H) = 160 Hz); 71.6 (d, ^1J(C,H) = 145 Hz); 58.1 (q, ^1J(C,H) = 140 Hz); 33.3 (t, ^1J(C,H) = 135 Hz); 25.9 (q, ^1J(C,H) = 130 Hz); 0.80, 0.60 (2q, ^1J(C,H) = 120 Hz). MS (CI, NH_3) m/z: 275 M^+ +1, 6), 274 (M^+, 1), 217 (M^+ -tBu, 18), 201 (9), 187 (17), 169 (18), 159 (M^+ -Si(tBu)Me_2, 7), 157 (4), 143 (7), 131 (6), 129 (7), 127 (6), 119 (5), 118 (9), 117 (79), 113 (12), 103 (14), 101 (14), 99 (6), 97 (5), 96 (8), 89 (49). (Found: M^+-C_4H_9, 217.0888. $C_{13}H_{26}O_4Si$-C_4H_9 requires 217.0896).

(1RS,2SR,3SR,4RS,6RS)-3-*exo*,6-*endo*-Dimethoxy-7-oxabicyclo[2.2.1]heptan-2-*endo*-ol (**41**). A solution of **40** (500 mg, 1.82 mmol) in dry THF (5 mL), was added dropwise to a stirred suspension of NaH (60 mg, 80% oil suspension, 2.0 mmol) in dry THF (5 mL) under Ar atm. The mixture was stirred until the production of H_2 ceased, then MeI (0.13 mL, 2.08 mmol) was added. At the end of the reaction (TLC control, silica gel, light petroleum/EtOAc 6:4), the mixture was diluted with Et_2O and H_2O. The two phases were separated and the organic one was washed with 1 M $Na_2S_2O_3$ and then with H_2O, and diluted with THF (15 mL). $(n\text{-}Bu)_4NF{\cdot}3H_2O$ (618 mg, 1.96 mmol) was added and the mixture was stirred overnight. At the end of the reaction (TLC control, silica gel, light petroleum/EtOAc 6:4) the mixture was filtered through silica gel, rinsing with Et_2O, concentrated under atm. pressure with a Vigreux column and purified by flash chromatography (silica gel, CH_2Cl_2/Et_2O 8:2) to afford 117 mg (37%), colourless oil. IR (film) ν: 3480 (br.), 2990, 2940, 2900, 2830, 1450 (br.), 1370, 1215, 1190, 1100, 1015, 980, 950, 925 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.36 (m, H-C(1), H-C(4)); 4.10 (m, H-C(2), H-C(6)); 3.34 (s, OMe); 3.33 (d, H-C(3), J = 2.0 Hz); 2.25 (ddd, H_{exo}-C(5), J = 6.5, 9.0, 13.0 Hz); 1.30 (dd, H_{endo}-C(5), J = 3.0, 13.0 Hz). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 90.1, 83.4 (2d, ^1J(C,H) = 150 Hz); 83.0 (d, ^1J(C,H) = 155 Hz); 82.0 (d, ^1J(C,H) = 160 Hz); 73.3 (d, ^1J(C,H) = 165 Hz); 58.7 (q, ^1J(C,H) = 145 Hz); 56.0 (q, ^1J(C,H) = 140 Hz); 33.3 (t, ^1J(C,H) = 135 Hz). MS (CI, NH_3) m/z: 175 (M^+ +1, 1), 143 (M^+ -OMe, 1), 142 (2), 130 (1), 115 (10), 114 (9), 113 (5), 111 (3), 101 (4), 89 (2), 100 (3), 99 (10), 98 (100), 89 (2), 88 (5), 87 (39), 85 (8), 84 (2), 83 (5), 82 (7), 81 (6), 75 (17), 74 (20), 72 (8), 71 (44). (Found: M^+, 174.0879. $C_8H_{14}O_4$ requires 174.0892).

(1SR,3RS,4RS,6RS)-3-*exo*,6-*endo*-Dimethoxy-7-oxabicyclo[2.2.1]heptan-2-one (**14**). A solution of **41** (100 mg, 0.574 mmol) in dry CH_2Cl_2 (3 mL) was added dropwise to a stirred suspension of PCC (200 mg, 0.928 mmol) and 3 Å molecular sieves in dry CH_2Cl_2 (3 mL) under Ar atm. at 20°C. At the end of the reaction (TLC control, silica gel, light petroleum/EtOAc 6:4) Et_2O (6 mL) was added and stirring was continued for an additional h. The mixture was filtered through silica gel, rinsing with Et_2O. Distillation of the solvent under atm. pressure with a 10 cm Vigreux column, left 80 mg (81%), colourless oil. IR (film) ν: 2990, 2940, 2910, 2830, 1770, 1460 (br.), 1355, 1215, 1190, 1105, 1015 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.61 (d, H-C(4), J = 6.0 Hz); 4.39 (d, H-C(2), J = 5.0 Hz); 4.00 (ddd, H-C(6), J = 2.0, 5.0, 9.0 Hz); 3.52 (s, OMe); 3.36 (s, H-C(3)); 3.28 (s, OMe); 2.36 (ddd, H_{exo}-C(5), J = 6.0, 9.0, 13.5 Hz); 1.53 (dd, H_{endo}-C(5), J = 2.0, 13.5 Hz). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 206.4 (s); 80.8, 80.4, 80.1 (3d, ^1J(C,H) = 165 Hz); 78.0 (d, ^1J(C,H) = 145 Hz); 58.3, 57.7 (2q, ^1J(C,H) = 145 Hz); 33.7 (t, ^1J(C,H) = 135 Hz). MS (CI, NH_3) m/z: 190 (M^+ +18, 0.4), 116 (2), 115 (3), 114 (1), 104 (17), 98 (4), 89 (2), 88 (1), 87 (2), 85 (5), 83 (1), 81 (2), 75 (3), 72 (6), 71 (100). (Found: M^+, 172.0710. $C_8H_{12}O_4$ requires 172.0735).

(1RS,2SR,3SR,4RS,5RS)-3-*endo*-t-Butyldimethylsilyl-5-*endo*-methoxy-7-oxabicyclo[2.2.1]heptan-2-*endo*-ol (**43**). A solution of **40** (1.738 g, 6.333 mmol) in dry CH_2Cl_2 (50 mL) was added dropwise to a stirred suspension of PCC (2.04 g, 9.50 mmol) and 3 Å molecular sieves in dry CH_2Cl_2 (50 mL) under Ar atm. at 20°C. At the end of the reaction (TLC control, silica gel, light petroleum/EtOAc 6:4), Et_2O (50 mL) was added and stirring was continued for an additional h. The mixture was then filtered through silica gel, rinsing with Et_2O. Distillation of the solvent under atm. pressure with a Vigreux column afforded 1.738 g of a yellow oil. The oil was dissolved in MeOH (20 mL) and $NaBH_4$ (259 mg, 97%, 6.41 mmol) was added portionwise while stirring at 20°C. The mixture was then diluted with H_2O and extracted with CH_2Cl_2 (30 mL, 3 times). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under atm. pressure with a Vigreux column to afford a colourless oil. Flash chromatographic purification of the oil (silica gel, CH_2Cl_2) gave 672 mg (39%), colourless oil. IR (film) ν: 3520 (br.), 2980, 2950, 2930, 2890, 2830, 1460, 1360, 1250,

1215, 1150, 1020 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.41 (dd, H-C(1), J = 6.0, 5.5 Hz); 4.26 (dd, H-C(4), J = 5.5, 5.5 Hz); 4.07 (dd, H-C(3), J = 5.5, 8.5 Hz); 4.05 (dddd, H-C(5), J = 1.5, 3.5, 5.0, 10.0 Hz); 3.94 (dddd, H-C(2), J = 1.5, 5.0, 8.5, 12.0 Hz); 3.17 (d, OH, J = 12.0 Hz); 3.31 (s, OMe); 2.14 (dd, H_{endo}-C(6), J = 3.5, 13.0 Hz); 1.90 (dddd, H_{exo}-C(6), J = 1.0, 6.0, 10.0, 13.0 Hz); 0.87 (s, t-Bu); 0.05, 0.02 (2s, Me_2Si). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 83.5 (d, ^1J(C,H) = 155 Hz); 81.7 (d, ^1J(C,H) = 150 Hz); 75.2 (d, ^1J(C,H) = 160 Hz); 72.0 (d, ^1J(C,H) = 155 Hz); 67.4 (d, ^1J(C,H) = 150 Hz); 58.3 (q, ^1J(C,H) = 145 Hz); 29.0 (t, ^1J(C,H) = 130 Hz); 27.5 (q, ^1J(C,H) = 130 Hz); 18.1 (s); 0.80, 0.50 (2q, ^1J(C,H) = 120 Hz). MS (CI, NH_3) m/z: 275 (M^+ +1, 5), 219 (2), 218 (5), 217 (35), 201 (3), 199 (3), 187 (4), 185 (7), 167 (8), 131 (10), 129 (14), 125 (26), 117 (48), 111 (18), 109 (4), 107 (9), 103 (8), 101 (15), 99 (10), 97 (10), 95 (10), 92 (5), 91 (5), 89 (27), 77 (11), 76 (9), 75 (100). (Found: M^+-C_4H_9, 217.0877. $C_{13}H_{26}O_4Si$-C_4H_9 requires 217.0896).

(1RS,2SR,3RS,4RS)-3-*endo*,6-*endo*-Dimethoxy-7-oxabicyclo[2.2.1]heptan-2-*endo*-ol (**44**). A solution of **43** (670 mg, 2.44 mmol) in dry THF (6 mL) was added dropwise to a stirred suspension of KH (100 mg, 2.44 mmol) in dry THF (4 mL). The mixture was stirred until the production of H_2 ceased, then MeI (0.2 mL, 3.2 mmol) was added and the solution was heated under reflux 3 d. The mixture was then diluted with H_2O and CH_2Cl_2. The two phases were separated and the aq. one was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under atm. pressure with a Vigreux column. The residue was dissolved in THF (10 mL) and (n-Bu)$_4$NF·3H_2O (800 mg, 2.54 mmol) was added. The mixture was stirred for 3 days. It was then filtered through silica gel, rinsing with Et_2O. The solvents were distilled off under atm. pressure with a Vigreux column and the residue was purified by flash chromatography (silica gel, CH_2Cl_2) to give 100 mg (23%), colourless oil. IR (film) ν: 3500 (br.), 2990, 2930, 2850, 1450, 1365, 1215, 1200, 1120, 1050, 1020, 970, 915 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.55 (m, H-C(4)); 4.31 (dd, H-C(1), J = 5.0, 5.0 Hz); 4.12 (m, H-C(6), H-C(2)); 3.96 (d, OH, J = 11.5 Hz); 3.67 (dd, H-C(3), J = 5.5, 8.5 Hz); 3.40, 3.36 (2s, 2 OMe); 2.02 (m, H_2C(5)). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 83.7 (d, ^1J(C,H) = 155 Hz); 80.1 (d, ^1J(C,H) = 160 Hz), 75.7 (d, ^1J(C,H) = 150 Hz); 74.7 (d, ^1J(C,H) = 160 Hz); 72.2 (d, ^1J(C,H) = 150 Hz); 58.6 (q, ^1J(C,H) = 145 Hz); 58.3 (q, ^1J(C,H) = 145 Hz); 29.0 (t, ^1J(C,H) = 135 Hz). MS (CI, NH_3) m/z: 183 (M^+ +19, 3), 154 (5), 150 (4), 143 (M^+ -OMe, 6), 127 (8), 121 (7), 113 (12), 111 (16), 110 (9), 108 (17), 106 (10), 105 (8), 99 (16), 98 (13), 97 (37), 96 (15), 95 (32), 93 (13), 85 (32), 84 (16), 83 (39), 82 (22), 81 (43), 79 (18), 78 (13), 77 (19), 75 (15), 73 (14), 72 (18), 71 (100).

(1SR,3SR,4RS,6RS)-3-*endo*,6-*endo*-Dimethoxy-7-oxabicyclo[2.2.1]heptan-2-one (**15**). A solution of **44** (83 mg, 0.48 mmol) in dry CH_2Cl_2 (2 mL) was added dropwise to a stirred suspension of PCC (110 mg, 0.510 mmol and 3 Å molecular sieves in dry CH_2Cl_2 (1 mL). At the end of the reaction (TLC control, silica gel, light petroleum/EtOAc 7:3) Et_2O (3 mL) was added and the mixture was stirred for an additional h, then it was filtered through silica gel, rinsing with CH_2Cl_2. Distillation of the solvent under atm. pressure with a Vigreux column afforded 70 mg (85%), colourless oil. IR (film) ν: 2930 (br.), 1770, 1460, 1350, 1220, 1205, 1110, 1020 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.77 (dd, H-C(4), J = 5.5, 5.5 Hz); 4.69 (d, H-C(1), J = 5.5 Hz); 4.12 (m, H-C(6)); 3.89 (d, H-C(3), J = 5.5 Hz); 3.52, 3.33 (2s, 2 OMe); 2.21 (m, H_{exo}-C(5)); 1.90 (dd, H_{endo}-C(5), J = 3.0, 13.0 Hz). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 206.0 (s); 82.1 (d, ^1J(C,H) = 150 Hz); 81.6 (d, ^1J(C,H) = 165 Hz); 80.1 (d, ^1J(C,H) = 155 Hz); 77.3 (d, ^1J(C,H) = 160 Hz); 59.1, 58.0 (2q, ^1J(C,H) = 145 Hz); 29.3 (t, ^1J(C,H) = 135 Hz). MS (CI, NH_3) m/z: 190 (M^+ +18, 0.2), 172 (M^+, 0.4), 141 (M^+ -OMe, 1), 116 (2), 115 (10), 114 (4), 112 (2), 111 (9), 104 (32), 71 (100). (Found: M^+, 172.0728. $C_8H_{12}O_4$ requires 172.0735).

(1RS,3SR,4SR,6SR)-6-*endo*-Benzyloxy-2-oxo-7-oxabicyclo[2.2.1]hept-3-*exo*-yl benzoate (**16**). A solution of alcohol **48** (100 mg, 0.43 mmol) and benzoic anhydride (100 mg, 0.44 mmol) in pyridine (2 mL) was stirred at 60°C for 24 h. At the end of the reaction (TLC control, silica gel, light petroleum/EtOAc 7:3) the solvents were distilled off under reduced pressure. The residue was diluted with EtOAc (10 mL) and washed with 5% aq. Na_2CO_3 (7 mL) and brine (7 mL). Then it was dried ($MgSO_4$), filtered and concentrated under reduced pressure to obtain 115 mg (79%), colourless oil. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 8.07 (m, C_6H_5); 7.72-7.24 (m, C_6H_5); 5.06 (s, H-C(2)); 4.79 (d, H-C(1), J = 6.0 Hz); 4.60 (d, -C*H*HPh, J = 11.0 Hz); 4.55 (d, H-C(4), J = 5.0 Hz); 4.48 (d, -CH*H*Ph, J = 11.0 Hz); 2.44 (ddd, H_{exo}-C(6), J = 6.0, 9.0, 13.5 Hz); 1.89 (dd, H_{endo}-C(6), J = 2.0, 13.5 Hz). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 203.3 (s,), 171.9 (s), 166.0 (s), 136.7 (s), 133.7 (d, ^1J(C,H) = 160 Hz); 133.6 (d, ^1J(C,H) = 160 Hz); 130.2 (d, ^1J(C,H) = 165 Hz); 130.0 (d, ^1J(C,H) = 165 Hz); 128.5 (d, ^1J(C,H) = 160 Hz); 128.4 (d, ^1J(C,H) = 160 Hz); 128.1 (d, ^1J(C,H) = 160 Hz); 128.0 (d, ^1J(C,H) = 160 Hz); 80.9 (d, ^1J(C,H) = 165 Hz); 75.6 (d, ^1J(C,H) = 155 Hz); 73.8 (d, ^1J(C,H) = 155 Hz); 72.3 (t, ^1J(C,H) = 145 Hz); 34.4 (t, ^1J(C,H) = 135 Hz).

(1RS,3SR,4SR,6SR)-6-*endo*-Benzyloxy-3-*exo*-[(t-butyl)dimethylsilyloxy]-7-oxabicyclo[2.2.1]heptan-2-one (**17**). A solution of (t-Bu)Me_2SiCl (370 mg, 2.43 mmol) in DMF (1.3 mL) was added dropwise to a solution of **48** (157 mg, 0.55 mmol) and imidazole (320 mg, 4.71 mmol) in DMF (5 mL) cooled at 0°C. After 2 h the

mixture was diluted with H_2O and ice (40 mL) and Et_2O (50 mL). The two phases were separated and the ethereal layer was washed with 5% aq. HCl (20 mL) and brine (20 mL). Then it was dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford a colourless oil. The oil was purified by chromatography (silica gel, light petroleum/EtOAc 3:2) to give 170 mg (89%), colourless oil. IR (CH_2Cl_2) v: 2940, 2920, 2880, 2850, 1770, 1510, 1175, 1090, 1025, 950, 855, 830 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 7.18 (m, Ph); 4.57 (d, -C*H*H, J = 11.5 Hz); 4.51 (d, H-C(4), J = 6.0 Hz); 4.43 (d, H-C(1), J = 4.5 Hz); 4.41 (d, -CH*H*-, J = 11.5 Hz); 4.19 (dddd, H-C(6), J = 1.0, 2.5, 4.5, 9.5 Hz); 3.77 (d, H-C(3), J = 1.0 Hz); 2.36 (ddd, H_{exo}-C(5), J = 6.0, 9.5, 13.5 Hz); 1.61 (dd, H_{endo}-C(5), J = 2.0, 13.5 Hz); 0.90 (s, t-Bu); 0.16, 0.13 (2s, Me_2Si). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 207.2, 136.9 (2s); 128.5 (s, ^1J(C,H) = 160 Hz); 128.0 (d, ^1J(C,H) = 160 Hz); 83.1 (d, ^1J(C,H) = 160 Hz); 80.0 (d, ^1J(C,H) = 165 Hz); 75.8 (d, ^1J(C,H) = 155 Hz); 74.4 (d, ^1J(C,H) = 150 Hz); 72.1 (t, ^1J(C,H) = 140 Hz); 34.1 (t, ^1J(C,H) = 135 Hz); 25.7 (q, ^1J(C,H) = 125 Hz); 18.3 (s); 0.8 (q, ^1J(C,H) = 120 Hz); 0.8 (q, ^1J(C,H) = 120 Hz): MS (CI, NH_3) m/z: 366 (M^+ +18, 1), 291 (M^+, - tBu, 4), 229 (1), 185 (5), 171 (3), 157 (2), 143 (2), 129 (4), 117 (10), 92 (5), 91 (100). Anal. calc. for $C_{19}H_{28}O_4Si$ (348.52): C 65.48, H 8.10; found: C 65.53, H 8.17.

(1RS,2SR,4SR)-6-Bromo-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl p-toluenesulfonate (**47**). A solution of **45**[11] (500 mg, 2.62 mmol) in pyridine (2 mL) was added dropwise to a stirred solution of p-toluenesulfonyl chloride (500 mg, 2.62 mmol) and 4-(dimethylamino)pyridine (DMAP 10 mg, 0.07 mmol) in pyridine (2 mL). Stirring was continued for 48 h. Then the solution was diluted with EtOAc (20 mL), washed successively with 5% HCL (20 mL, twice), 5% aq. $NaHCO_3$ (20 mL) and brine (20 mL), dried ($MgSO_4$), filtered and concentrated. Column chromatography (silica gel, light petroleum/Et_2O 3:2) afforded 460 mg (51%), of the tosylate **47** and 90 mg (18%) of the alcohol **45**. Characteristics of **47**: colourless crystals, m.p. 83.5-84.5°C. IR (KBr) v: 3100, 3060, 3010, 1580, 1360, 1355, 1290, 1170, 1010, 985, 865, 840, 810 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 7.82, 7.36 (m, 4H); 6.60 (d, H-C(5), J = 2.0 Hz); 5.05 (ddd, H-C(2), J = 2.0, 4.5, 8.0 Hz); 4.89 (dd, H-C(4), J = 2.0, 4.5 Hz); 4.80 (d, H-C(1), J = 4.5 Hz); 2.46 (s, Me); 2.27 (ddd, H_{exo}-C(3), J = 4.5, 8.0, 12.5 Hz); 1.39 (dd, H_{endo}-C(3), J = 2.0, 12.5 Hz). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 145.1 (s); 136.5 (d, ^1J(C,H) = 185 Hz); 132.9 (s); 129.9 (d, ^1J(C,H) = 160 Hz); 127.9 (d, ^1J(C,H) = 170 Hz); 122.2 (s); 81.8 (d, ^1J(C,H) = 170 Hz); 80.9 (d, ^1J(C,H) = 165 Hz); 74.9 (d, ^1J(C,H) = 160 Hz); 32.8 (t, ^1J(C,H) = 140 Hz); 21.6 (q, ^1J(C,H) = 125 Hz). MS (70 eV) m/z: 198 (5), 192 (3), 191 (M^+ -SO_2PhMe, 33), 194 (4), 189 (M^+ -SO_2PhMe, 34), 188 (2), 161 (4), 159 (3), 157 (4), 156 (5), ($^+SO_2$PhMe, 67), 149 (8), 148 (41), 147 (8), 146 (40), 139 (3), 133 (2), 119 (3), 92 (10), 91 (100), 89 (11), 82 (17), 81 (11), 77 (4), 66 (7), 65 (43), 64 (4), 63 (11), 62 (2), 53 (32), 52 (5), 51 (15). Anal. calc. for $C_{13}H_{13}BrO_4S$ (345.24): C 45.23, H 3.80, Br 23.15; found: C 45.04, H 3.69, Br 23.15.

5-*exo*-Hydroxy-6-oxo-7-oxabicyclo[2.2.1]hept-2-*endo*-yl p-toluenesulfonate (**49**). $NaHCO_3$ (111 mg, 1.74 mmol), OsO_4 (0.15 mL, sol. 0.5 M in CCl_4, 0.08 mmol) in 30% H_2O_2 (0.6 mL), 5.5 mmol) were added in succession to a stirred soution of **47** (300 mg, 0.869 mmol) in THF (12 mL). The solution was then stirred for an additional h at 0°C then allowed to warm to 20°C. At the end of the reaction (silica gel, light petroleum/EtOAc 7:3) the mixture was diluted with EtOAc (30 mL), washed with 5% aq. Na_2SO_3 (15 mL, 3 times) and then with brine (15 mL), dried ($MgSO_4$), filtered and concentrated in vacuo to give a yellow oil (260 mg). The oil was crystallized from Et_2O at -30°C to afford 130 mg (50%) colourless crystals, m.p. 96-97°C. IR (KBr) v: 3470 (br.), 3060, 3010, 2960, 2930, 1770, 1600, 1490, 1450, 1355, 1295, 1250, 1180, 1175, 1090, 1030, 990, 910, 870, 810, 790, 760, 670 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 7.77, 7.36 (m, 4H); 4.94 (ddd, H-C(2), J = 2.5, 5.5, 10.0 Hz); 4.64 (d, H-C(4), J = 6.5 Hz); 4.29 (d, H-C(1), J = 5.5 Hz); 3.77 (s, H-C(5)); 2.51 (ddd, H_{exo}-C(3), J = 6.5, 10.0, 14.5 Hz); 2.45 (s, Me), 1.76 (dd, H_{endo}-C(3), J = 2.5, 14.5). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 209.5, 145.7, 136.5 (3s); 130.1, 128.1, 82.1 (3d, ^1J(C,H) = 165 Hz); 78.7 (d, ^1J(C,H) = 175 Hz); 74.8 (d, ^1J(C,H) = 160 Hz); 73.2 (d, ^1J(C,H) = 150 Hz); 33.5 (t, ^1J(C,H) = 135 Hz); 21.6 (q, ^1J(C,H) = 130 Hz). MS (CI, NH_3) m/z: 316 (M^+ +18, 24), 298 (M^+, 0.4), 205 (3), 191 (3), 190 (7), 189 (2), 171 (2), 157 (5), 156 (7), 155 ($^+SO_2$PhMe, 79), 146 (2), 127 (4), 125 (16), 108 (15), 99 (12), 98 (67), 97 (17), 93 (14), 92 (37), 91 (100), 89 (17), 81 (10). Analc. calc. for $C_{13}H_{14}O_6S$ (289.31): C 52.34, H 4.73; found: C 52.25, H 4.70.

3-Oxo-5-*endo*-p-toluenesulfonyl-7-oxabicyclo[2.2.1]hept-2-*exo*-yl acetate (**18**). A mixture of **49** (521 mg, 1.75 mmol), pyridine (5 mL), acetic anhydride (1 mL) and DMAP (catalytic quantity) was stirred for 12 h. At the end of the reaction (TLC control, silica gel, light petroleum/EtOAc 6:4) the mixture was diluted with EtOAc (40 mL), washed successively with 5% HCl (20 mL, twice), H_2O (20 mL) and brine (20 mL), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was diluted with CH_2Cl_2 and filtered through silica gel. Distillation of the solvent under reduced pressure, followed by crystallization from light petroleum/EtOAc afforded 237 mg (42%) white crystals, m.p. 111-114°C. IR (KBr) v: 3040, 2960, 2930, 1780, 1745, 1500, 1365, 1300, 1230, 1210, 1190, 1175, 1095, 1070, 1035, 1010, 1000, 945, 910, 895, 835, 820, 785, 770, 680, 665 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 7.77, 7.36 (m, 4H); 5.00 (ddd, H-C(2), J = 2.5, 5.5, 9.5 Hz); 4.72 (s, H-C(5)); 4.65 (d, H-C(1), J = 6.0 Hz); 4.36 (d, H-C(4), J = 5.5 Hz); 2.53 (ddd, H_{exo}-C(3), J = 6.0, 9.5,

14.5 Hz); 2.44, 2.12 (2s, 2 Me); 1.85 (dd, H_{endo}-C(3), J = 2.5, 14.5 Hz). MS (CI, NH_3) m/z: 342 (M^+ +19, 23), 341 (M^+ +18, 100), 190 (9), 185 (7), 168 (5), 156 (4), 155 (M^+ -OTos, 34), 140 (8), 125 (32), 108 (13), 98 (9), 92 (9), 91 (39).

Baeyer-Villiger oxidations with 3-$ClC_6H_4CO_3H$. A solution of mCPBA (96%, 0.07 mmol) in $CDCl_3$ (0.5 mL) was added dropwise in a NMR tube containing the ketone **9-18** (0.07 mmol), $NaHCO_3$ (0.07 mmol) and $CDCl_3$ (0.5 mL). The reaction was followed by ^{1}H-NMR. In the cases where lactones (see Table) were isolated, the mixture was diluted with CH_2Cl_2, washed with 5% $NaHCO_3$ and brine, dried ($MgSO_4$), filtered and concentrated with a Vigreux column under atm. pressure.
Baeyer-Villiger oxidations with CH_3CO_3H. A solution of CH_3CO_3H (32% in H_2O, 0.07 mmol) in $CDCl_3$ (0.5 mL), was added dropwise to a stirred solution of the ketone **9-18** (0.07 mmol) and NaOAc (0.07 mmol) in $CDCl_3$ (0.5 mL). At the end of the reaction (TLC control, silica gel), the mixture was filtered through a 3 mm layer of silica gel directly in a NMR tube. In the cases where lactones were isolated, the mixture was diluted with CH_2Cl_2, washed with 5% aq. $NaHCO_3$ then with brine, dried ($MgSO_4$), filtered and concentrated with a Vigreux column under atm. pressure.

Characteristics of 2,8-Dioxabicyclo[3.2.1]octan-3-one (**50**). IR (film) ν: 3000, 2980, 2960, 1740, 1380, 1335, 1205, 1155, 1070, 1045, 990, 950 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 5.87 (dd, H-C(1), J = 1.0, 3.0 Hz); 4.73 (ddd, H-C(5), J = 0.5, 6.0, 6.0 Hz); 2.95 (ddd, H_{exo}-C(4), J = 2.0, 6.0, 18.0 Hz); 2.38 (d, H_{endo}-C(4), J = 18.0 Hz); 2.32-2.01, 1.87-1.80 (m, H_2-C(6), H_2-C(7)). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 166.7 (s); 102.3 (d, ^1J(C,H) = 185 Hz), 73.8 (d, ^1J(C,H) = 160 Hz); 39.4 (t, ^1J(C,H) = 130 Hz); 35.5 (t, ^1J(C,H) = 135 Hz); 26.9 (t, ^1J(C,H) = 135 Hz). MS (EI) m/z: 129 (M^+ +1, 79), 128 (M^+, 32), 111 (100), 106 (5), 100 (2), 84 (18), 83 (7). (Found: M^+, 128.0468. $C_6H_8O_3$ requires 128.0473).

Characteristics of 4-*exo*-methoxy-3,8-dioxabicyclo[3.2.1]octan-2-one (**53**). ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.89 (s, H-C(4)); 4.66, 4.46 (dd, H-C(1), H-C(5), J = 6.0 Hz); 3.58 (s, OMe); 2.46-1.79 (m, H_2-C(6), H_2-C(7)).

Characteristics of 4-*exo*-methoxy-2,8-dioxabicyclo[3.2.1]octan-3-one (**52**). ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 5.94 (d, H-C(1), J = 4.0 Hz); 4.79 (d, H-C(5), J = 8.0 Hz); 3.49 (s, H-C(4), OMe); 2.46-1.62 (m, H_2-C(6), H_2-C(7)). (Found: M^+, 128.0468. $C_6H_8O_3$ requires 128.0473).

4-*endo*-[(t-Butyl)dimethylsilyloxy]-3,8-dioxabicyclo[3.2.1]octan-2-one (**57**). IR (CH_2Cl_2) ν: 2960, 2930, 1750, 1465, 1385, 1250, 1215, 1170, 1130, 1080, 1000, 960 cm^{-1}. ^{1}H-NMR (250 MHz, CD_2Cl_2) δ_H: 5.89 (d, H-C(4), J = 3.5 Hz); 4.55 (d, H-C(1), J = 7.0 Hz); 4.35 (ddd, H-C(5), J = 2.0, 3.5, 8.0 Hz); 2.36 (dddd, H_{exo}-C(6), J = 6.0, 7.0, 9.0, 12.0 Hz); 2.02 (m, H_{endo}-C(6), H_2-C(7)); 0.95 (s, t-Bu); 0.22, 0.20 (2s, S, Me). ^{13}C-NMR (62.9 MHz, CD_2Cl_2) δ_C: 169.0 (s); 97.4 (d, ^1J(C,H) = 170 Hz); 75.8 (d, ^1J(C,H) = 155 Hz); 74.7 (d, ^1J(C,H) = 165 Hz); 29.3 (t, ^1J(C,H) = 130 Hz); 25.7 (q, ^1J(C,H) = 125 Hz); 20.1 (t, ^1J(C,H) = 130 Hz); 181.1 (s); -4.39 (q, ^1J(C,H) = 120 Hz); -5.31 (q, ^1J(C,H) = 120 Hz): MS (CI, NH_3) m/z: 277 (M^+ +19, 14), 276 (M^+ +18, 49), 260 (M^+ +2, 24), 259 (M^+ +1, 100), 258 (M^+, 1), 201 (4), 173 (5), 157 (4), 144 (3), 131 (1), 129 (3). (Found: M^+-C_4H_9, 201.0598. $C_{12}H_{22}O_4Si$-C_4H_9 requires 217.0896).

4-*endo*-Methoxy-3,8-dioxabicyclo[3.2.1]octan-2-one (**59**). IR (film) ν: 2960 (br.), 2850, 1750, 1465, 1460, 1390, 1305, 1240, 1205, 1130, 1080, 1055, 995, 960, 910, 870 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 5.34 (d, H-C(4), J = 3.5 Hz); 4.51 (d, H-C(1), J = 7.0 Hz); 4.37 (ddd, H-C(5), J = 1.5, 3.5, 7.5 Hz); 3.50 (s, OMe); 2.28-1.76 (m, H_2-C(6), H_2-C(7)). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 169.7 (s), 103.0 (d, ^1J(C,H) = 175 Hz); 74.3 (d, ^1J(C,H) = 165 Hz), 73.5 (d, ^1J(C,H) = 155 Hz); 56.9 (q, ^1J(C,H) = 145 Hz); 28.5 (t, ^1J(C,H) = 135 Hz); 20.3 (t, ^1J(C,H) = 135 Hz). MS (CI, NH_3) m/z: 159 (M^+ +1, 10), 131 (4), 127 (M^+ -OMe, 2), 114 (2), 113 (5), 101 (8), 99 (28), 98 (13), 97 (5), 95 (3), 87 (4), 86 (57), 85 (11), 84 (70), 83 (3), 82 (5), 81 (17), 74 (2) 73 (3), 72 (5), 71 (87), 70 (100). (Found: M^+, 158.0569. $C_7H_{10}O_4$ requires 158.0579).

(1RS,4RS,5RS,7SR)-4-*exo*,7-*endo*-Dimethoxy-3,8-dioxabicyclo[3.2.1]octan-2-one (**61**). IR (film) ν: 2990, 2940, 2840, 1760, 1450, 1390, 1370, 1255, 1220, 1180, 1125, 1220, 1180, 1125, 1090, 1025, 970, 955, 950, 930, 730 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.98 (s, H-C(4)); 4.72 (d, H-C(1), J = 6.5 Hz); 4.31 (dd, H-C(5), J = 1.5, 8.5 Hz); 4.19 (ddd, H-C(7), J = 4.5, 6.5, 10.5 Hz); 3.58, 3.37 (2s, 2 OMe); 2.53 (ddd, H_{exo}-C(6), J 8.5, 10.0, 14.0 Hz); 1.77 (ddd, H_{endo}-C(6), J = 1.5, 4.5, 14.0 Hz). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 164.4 (s); 103.7 (d, ^1J(C,H) = 175 Hz); 80.6 (d, ^1J(C,H) = 155 Hz); 77.0, 74.3 (2d, ^1J(C,H) = 160 Hz); 58.6, 56.6 (2q, ^1J(C,H) = 145 Hz); 32.0 (t, ^1J(C,H) = 135 Hz). MS (CI, NH_3) m/z: 189 (M^+ +1, 1), 149 (2), 129 (5), 115 (6), 111 (10), 109 (7), 100 (25), 97 (17), 96 (10), 95 (16), 85 (27), 83 (22), 82 (14), 81 (23), 74 (14), 71 (100).

(1RS,4SR,5SR,7SR)-4-*endo*,7-*endo*-Dimethoxy-3,8-dioxabicyclo[3.2.1]octan-2-one (**63**). ^{1}H-NMR (250 MHz, $CDCl_3$) of the crude reaction mixture: δ_H: 5.43 (d, H-C(4), J = 3.5 Hz); 4.65 (d, H-C(1), J = 6.5 Hz); 4.30 (ddd, H-C(5), J = 2.0, 3.5, 5.5 Hz); 4.12 (ddd, H-C(7), J = 4.5, 6.5, 10.5 Hz); 3.58, 3.39 (2s, 2 OMe); 2.31 (ddd, H_{exo}-C(5), J = 8.0, 10.5, 15.0 Hz); 2.21 (ddd, H_{endo}-C(5), J = 2.0, 4.5, 15.0 Hz).

(1RS,4RS,5RS,7RS)-7-*endo*-Benzyloxy-3-oxo-2,8-dioxabicylco[3.2.1]octa-4-*exo*-yl benzoate (**64**). IR (CH_2Cl_2) ν: 3050, 2880-2860, 1765, 1745, 1210, 1090 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 8.09-7.43 (m, 10H, Ph); 5.93 (d, H-C(1), J = 3.5 Hz); 5.43 (s, H-C(5)); 4.69 (d, H-C(4), J = 7.0 Hz); 4.65 (d, -C*H*HPh, J = 11.0 Hz); 4.48 (d, -CH*H*Ph, J = 11.0 Hz); 4.29 (dd, H-C(2), J = 3.5, 3.5, 10.0 Hz); 2.47 (ddd, H_{exo}-C(3), J = 7.0, 10.0, 14.0 Hz); 1.85 (dd, H_{endo}-C(3), J = 3.5, 14.0 Hz).

(1RS,4SR,5SR,7SR)-7-*endo*-Benzyloxy-4-*exo*-[(t-butyl)dimethylsilyloxy]-3,8-dioxabicyclo[3.2.1]octan-2-one (**67**). IR (KBr) ν: 3040, 2080, 2070, 1745, 1725, 1595, 1435, 1370, 1345, 1235, 1190, 1170, 1130, 1095, 1050, 1015, 960, 955, 930, 900, 850, 810, 780, 750, 660 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 7.32 (m Ph); 5.36 (s, H-C(4)); 4.75 (d, H-C(1), J = 6.5 Hz); 4.69 (d, -C*H*H-, J = 11.0 Hz); 4.44 (d, -CH*H*, J = 11.0 Hz), 4.38 (ddd, H-C(7), J = 4.5, 6.5, 10.0 Hz); 4.19 (dd, H-C(5), J = 1.5, 8.5 Hz); 2.51 (ddd, H_{exo}-C(6), J = 8.5, 10.0, 14.0 Hz); 1.80 (ddd, H_{endo}-C(6), J = 1.5, 4.5, 11.0 Hz); 0.90 (s, tBu); 0.19, 0.15 (2s, Me_2Si). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 199.1 (s); 128.5 (d, ^1J(C,H) = 160 Hz); 128.2 (d, ^1J(C,H) = 160 Hz); 128.0 (d, ^1J(C,H) = 160 Hz); 98.3 (d, ^1J(C,H) = 170 Hz); 78.5 (d, ^1J(C,H) = 155 Hz); 77.2 (d, ^1J(C,H) = 160 Hz); 76.3 (d, ^1J(C,H) = 135 Hz); 73.1 (t, ^1J(C,H) = 145 Hz); 32.1 (t, ^1J(C,H) = 135 Hz); 29.7 (s); 25.6 (q, ^1J(C,H) = 125 Hz); 0.8 (q, ^1J(C,H) = 130 Hz); 0.6 (q, ^1J(C,H) = 130 Hz). MS (CI, NH_3) m/z: 365 (M^+ +1, 2), 364 (M^+, 1), 307 (M^+ -tBu, 4), 171 (2), 143 (4), 132 (2), 131 (2), 129 (2), 105 (9), 92 (9), 91 (100), 77 (5), 75 (17), 73 (16).

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