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The Baeyer-Villiger Oxidation of 8-Oxabicyclo[3.2.1]octan-3-ones. Substituent Effects on the Regioselectivity[1,2]

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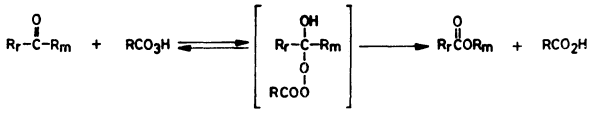
8-Oxabicyclo[3.2.1]octan-3-one derivatives serve as excellent models that elucidate factors controlling the reactivities and selectivities in the Baeyer-Villiger oxidation. The regioselectivity of the oxidation with trifluoroperacetic acid is markedly affected by the electronic properties of substituents at position α or β to the carbonyl function. Remote effects of the γ-substituents are also of significance. This study has disclosed yet unrecognized through-bond electronic influence and regioselection based on chiral orientation of hydroxyl group in the transient tetrahedral intermediate.

Oxidation of ketones by peroxy acids (Baeyer-Villiger reaction)[3] proceeds by way of transient tetrahedral intermediates,[4] which undergo fragmentation to give esters and carboxylic acids. Migration of R_m (sp^3)



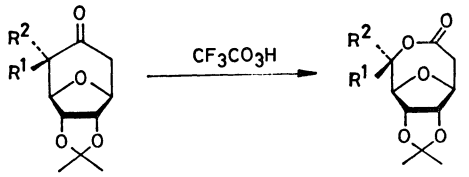
R_m=migrating group
R_r=remaining group

group to the adjacent electron-deficient oxygen atom occurs in a concerted manner with retention of configuration. The migratory aptitude appears to be related to the ability of a group to support a positive charge developing in the transition state.[5] Besides such electronic effects, conformational factors are also important in determining the regiochemistry.[6] 8-Oxabicyclo[3.2.1]octan-3-one structures serve as excellent models for examining factors which control the reactivity and selectivity in the reaction, because the C_s symmetry incorporated in the basic skeleton is not distorted to any great extent by introduction of substituents. In connection with our program of *C*-nucleoside synthesis,[7] we had an opportunity of examining the oxidation of a series of the substituted oxabicyclic ketones and found several unique substituent effects.

Results and Discussion

The oxidation of the ketonic substrates was carried out in dichloromethane at 15—25 °C by using three- to seven-fold excess of trifluoroperacetic acid in the presence of anhydrous disodium hydrogenphosphate. Most reaction proceeded smoothly, but the reaction mixture was routinely stirred for 10—36 h to ensure the completion. The structures of the products were elucidated by spectroscopic methods, particularly ^{1}H NMR measurement. The isomeric ratio of the products was conveniently determined by ^{1}H NMR or high-performance liquid chromatography (HPLC) analysis.

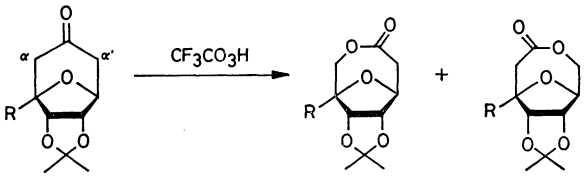
Reaction of the α-Substituted Ketones. The Baeyer-Villiger oxidation of the α-substituted ketones, **1**—**3**, proceeded rapidly and, as expected,[3] only single lactonic isomers, **5**—**7**, were obtained in high yield.[8] In a like manner, oxidation of the dimethylated ketone **4** afforded the lactone **8** as a sole product. The complete regioselectivity is based on the positive charge-stabilizing ability of the alkyl or phenyl group at position α to the carbonyl function.



1, $R^1=CH_3$; $R^2=H$
2, $R^1=n\text{-}C_5H_{11}$; $R^2=H$
3, $R^1=C_6H_5$; $R^2=H$
4, $R^1=R^2=CH_3$

5, $R^1=CH_3$; $R^2=H$
6, $R^1=n\text{-}C_5H_{11}$; $R^2=H$
7, $R^1=C_6H_5$; $R^2=H$
8, $R^1=R^2=CH_3$

Reaction of the β-Substituted Ketones. This class of compounds afforded a mixture of the regioisomeric lactones.[9] ^{1}H NMR spectra of the products arising from α-carbon migration exhibited an AB quartet due to the CH_2OCO protons, whereas the spectra of the α′-migrated isomers showed the same pattern of signals at higher field due to the CH_2COO protons. β-Alkyl substituents appear to direct the regiochemistry to only slight extent, giving the α- and α′-migration products in nearly equal amounts (Table 1). However, introduction of phenyl group which possesses ability of stabilizing positive charge partially developing at the α-methylene group resulted in greater α/α′ ratio, **14a**/**14b**=88:12.[10,11]



9, R=CH_3
10, R=$n\text{-}C_5H_{11}$
11, R=C_6H_5

12a, R=CH_3 **12b**, R=CH_3
13a, R=$n\text{-}C_5H_{11}$ **13b**, R=$n\text{-}C_5H_{11}$
14a, R=C_6H_5 **14b**, R=C_6H_5

Reaction of the γ-Substituted Ketones. In the course of study of oxidation of a variety of the γ-substituted bicyclo ketones, we observed yet unrecognized remote substituent effects.

A. Remote Electronic Effects. Reaction of the ketones, **15**—**22**, and trifluoroperacetic acid gave mixtures of the corresponding α-and α′-migration products

Table 1. Reaction of the β-substituted ketones[a)]

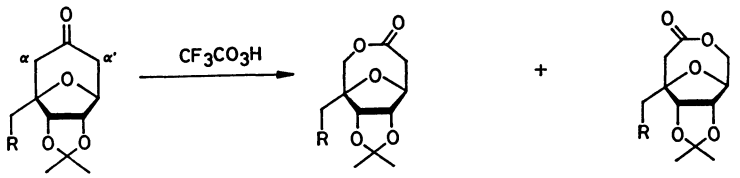
Ketone		CF_3CO_3H (equiv)	Temp °C	Time h	Lactone product	
No.	β-Substituent, R				Yield/%[b)]	**a**/**b** ratio[c)]
9	CH_3	3	20	10	90	53 : 47
10	n-C_5H_{11}	7	20	15	91	50 : 50
11	C_6H_5	5	25	12	93	88 : 12

a) Reaction with CF_3CO_3H in CH_2Cl_2. b) Isolated yield. c) Determined by ^1H NMR analysis.

Table 2. Reaction of the γ-substituted ketones.[a)] Remote electronic effects on the regioselectivity

Ketone		^{13}C NMR shift of C=O[b)]	Lactone product	
No.	β-Substituent, R		Yield/%[c)]	**a**/**b** ratio[d)]
15	$OSi(CH_3)_2$-t-C_4H_9	205.85	100	55 : 45
9	H	205.59	90	53 : 47
10	n-C_4H_9	205.88	91	50 : 50
16	$OCH_2C_6H_5$	205.41	83	48 : 52
17	$OCOCH_3$	204.19	80	35 : 65
18	OCO-t-C_4H_9	204.44	91	31 : 69
19	$OCOC_6H_5$	204.49	100	28 : 72
20	$OCOCF_3$	203.34	98	23 : 77
21	OSO_2CH_3	203.62	93	19 : 81
22	OSO_2CF_3	202.74	89	14 : 86
8-Oxabicyclo[3.2.1]octan-3-one		206.67	—	—
33	$OCH_2C_6H_5$	205.66	81	30 : 70
34	$OSi(CH_3)_2$-t-C_4H_9	205.76	93	30 : 70
35	$OCOCH_3$	204.78	78	46 : 54
36	OCO-t-C_4H_9	204.77	89	35 : 65
37	$OCOC_6H_5$	204.86	95	35 : 65

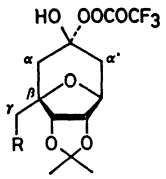
a) Reaction with 3 equiv of CF_3CO_3H in CH_2Cl_2 at 25 °C (for **15**—**22**) or at 15 °C (for **33**—**37**) for 12 h. For **9**, 3 equiv of CF_3CO_3H at 20 °C for 10 h. For **10**, 7 equiv of CF_3CO_3H at 20 °C for 15 h. b) In $CDCl_3$ with $(CH_3)_4Si$ as internal standard. c) Isolated yield. d) ^1H NMR determination for the reaction with **15**—**22**. HPLC analysis for the reaction with **33**—**37**.



15, R=$OSi(CH_3)_2$-t-C_4H_9 **23a**, R=$OSi(CH_3)_2$-t-C_4H_9 **23b**, R=$OSi(CH_3)_2$-t-C_4H_9
16, R=$OCH_2C_6H_5$ **24a**, R=$OCH_2C_6H_5$ **24b**, R=$OCH_2C_6H_5$
17, R=$OCOCH_3$ **25a**, R=$OCOCH_3$ **25b**, R=$OCOCH_3$
18, R=OCO-t-C_4H_9 **26a**, R=OCO-t-C_4H_9 **26b**, R=OCO-t-C_4H_9
19, R=$OCOC_6H_5$ **27a**, R=$OCOC_6H_5$ **27b**, R=$OCOC_6H_5$
20, R=$OCOCF_3$ **28a**, R=$OCOCF_3$ **28b**, R=$OCOCF_3$
21, R=OSO_2CH_3 **29a**, R=OSO_2CH_3 **29b**, R=OSO_2CH_3
22, R=OSO_2CF_3 **30a**, R=OSO_2CF_3 **30b**, R=OSO_2CF_3

in 80—100% yield. As is seen from Table 2, the isomeric ratio is highly dependent on the nature of γ-substituent R. The general trend indicates that the regioselectivity is determined by remote electronic effects of R group. Model inspection provides no indication for significance of steric or conformational factors. Notably electron-accepting substituents favor the α'-carbon migration over the α-carbon rearrangement. The relative α'-directing capabilities decrease in the order of OSO_2R > OCOR > OR > alkyl or H; OSO_2CF_3 > OSO_2CH_3; $OCOCF_3$ > $OCOC_6H_5$ > $OCOCH_3$; $OCH_2C_6H_5$ > $OSi(CH_3)_2$-t-C_4H_9. By contrast, electron-donating groups exhibited slight preference for the α-migration. The feeble but definite α-selection observed with **9** is to be noted. The well-known Si^+O^- polarization[12)] also resulted in some α-regioselection. These findings can be rationalized by considering the mode of transmission of through-

bond electronic effects.[13] The C(γ)–R bond polarization caused by an electronegative R group decreases electron density of the γ-and α-positions in the tetrahedral intermediate **31**, whereas an electron-donating R group makes these two carbon atoms more eletropositive. The α-position is unaffected through such electronic perturbation. As a consequence, the observed regiochemical bias is resulted.



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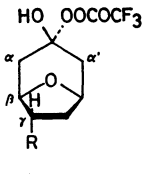
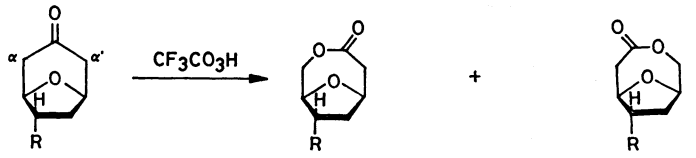


32

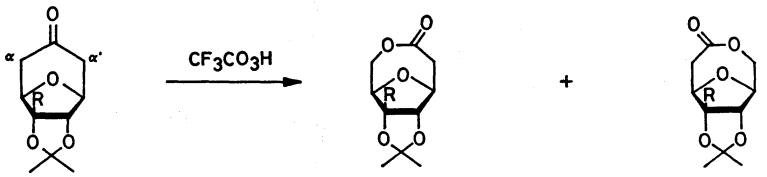
This type of induced electronic directing effect was noticed also in the oxidation of the ketones **33**—**37** which proceeds *via* the intermediate **32** (Table 2). The structures, **38a**—**42a** and **38b**—**42b**, were readily differentiated by ^{1}H NMR; the isomers of **a** series gave the C*H*R signal at a lower field than the **b** regioisomers owing to the anisotropic effect of the lactone oxygen atom. Thus electron-withdrawing groups attached to the γ-carbon atom showed a moderate degree of α'-regioselection. Here the substituent effects would be less straightforward, because (1) R group in **32** is accommodated in the seven-membered ring and exerts electronic influence not only the α-carbon but also the α'-position, though less effectively, and (2) the R–C(γ)–C(β)–C(α) backbone is distorted to some extent from normal zig-zag arrangement. Nevertheless the observed regioselectivity is compatible qualitatively with the above described interpretation.

These unprecedented remote interactions between the directing substituent and the migrating group should be a reflection of the regidity of the σ framework that facilitates the through-bond electronic influence. Some indication for the efficiency of electronic transmission in these systems may be offered by ^{13}C NMR measurement of the parent ketones; the carbonyl carbon signal appears to move *upfield* considerably with an increase in electron-withdrawing ability of γ-substituents (Table 2).

B. Steric Effects. Oxidation of the oxabicyclic ketones **43**—**50** with trifluoroperacetic acid was examined, and the structures of the regioisomeric lactone products were verified again easily by ^{1}H NMR as the case with the reaction of **33**—**37**. Here ease with which the oxidation takes place was found to be influenced profoundly by bulkiness of the substituent having endo configuration. The parent ketone (R= H) was readily transformed to the lactone, but introduction of methyl group, for instance, reduced the reaction rate by a factor of 4, as revealed by a competition experiment. The *t*-butyl derivative **45** was totally inert to the peroxy acid oxidation. This is obviously ascribable to steric screening effect of R group. Nucleophilic addition of trifluoroperacetic acid to the bicyclic ketones is expected to occur stereoselectively from the less hindered side[14] and, therefore, formation of the tetrahedral adducts of type **58** would be retarded by the presence of a bulky R group which introduces substantial steric repulsion with the hydroxyl.



33, R=$OCH_2C_6H_5$	**38a**, R=$OCH_2C_6H_5$	**38b**, R=$OCH_2C_6H_5$
34, R=$OSi(CH_3)_2$-*t*-C_4H_9	**39a**, R=$OSi(CH_3)_2$-*t*-C_4H_9	**39b**, R=$OSi(CH_3)_2$-*t*-C_4H_9
35, R=$OCOCH_3$	**40a**, R=$OCOCH_3$	**40b**, R=$OCOCH_3$
36, R=OCO-*t*-C_4H_9	**41a**, R=OCO-*t*-C_4H_9	**41b**, R=OCO-*t*-C_4H_9
37, R=$OCOC_6H_5$	**42a**, R=$OCOC_6H_5$	**42b**, R=$OCOC_6H_5$



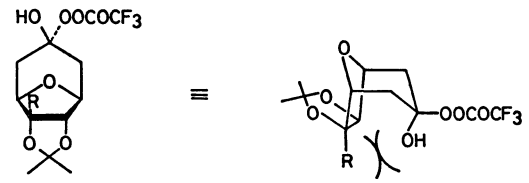
43, R=CH_3	**51a**, R=CH_3	**51b**, R=CH_3
44, R=*n*-C_5H_{11}	**52a**, R=*n*-C_5H_{11}	**52b**, R=*n*-C_5H_{11}
45, R=*t*-C_4H_9	—	—
46, R=C_6H_5	**53a**, R=C_6H_5	**53b**, R=C_6H_5
47, R=$CH_2OSi(CH_3)_2$-*t*-C_4H_9	**54a**, R=$CH_2OSi(CH_3)_2$-*t*-C_4H_9	**54b**, R=$CH_2OSi(CH_3)_2$-*t*-C_4H_9
48, R=$CH_2OCH_2C_6H_5$	**55a**, R=$CH_2OCH_2C_6H_5$	**55b**, R=$CH_2OCH_2C_6H_5$
49, R=CH_2OCO-*t*-C_4H_9	**56a**, R=CH_2OCO-*t*-C_4H_9	**56b**, R=CH_2OCO-*t*-C_4H_9
50, R=$CH_2OCOC_6H_5$	**57a**, R=$CH_2OCOC_6H_5$	**57b**, R=$CH_2OCOC_6H_5$

Table 3. Reaction of the γ-substituted ketones.[a] Steric effects on the regioselectivity

Ketone		Conversion/%	Lactone product	
No.	β-Substituent, R		Yield/%[b]	**a**/**b** ratio[c]
43	CH_3	62	84	33 : 67[d]
44	n-C_5H_{11}	48	85	25 : 75[d]
45	t-C_4H_9	0	—	—
46	C_6H_5	19	82	39 : 61[d]
47	$CH_2OSi(CH_3)_2$-t-C_4H_9	38	94	26 : 74
48	$CH_2OCH_2C_6H_5$	32	76	23 : 77
49	CH_2OCO-t-C_4H_9	46	82	34 : 66
50	$CH_2OCOC_6H_5$	28	75	40 : 60

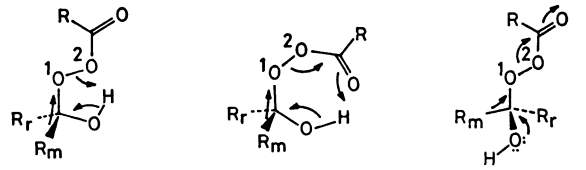
a) Reaction with 3 equiv of CF_3CO_3H in CH_2Cl_2 at 20 °C for 36 h (for **43**, at 25 °C for 36 h). b) Isolated yield. Based on consumed starting material. c) Determined by HPLC analysis. d) Obtained by ^1H NMR analysis.

In usual, rate-determining step of the Baeyer-Villiger oxidation has been considered to be the fragmentation of the tetrahedral intermediate,[15] but in the present case equilibrium concentration of the intermediate **58** is also important.[16]

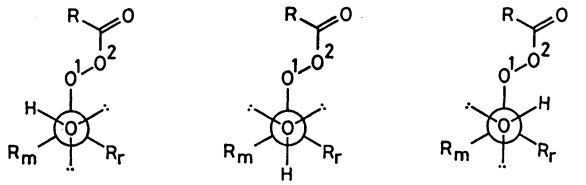


58

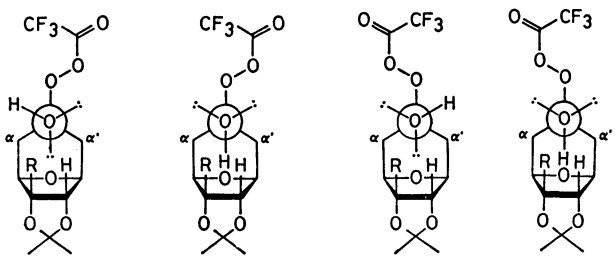
Regioselectivity is also affected by the γ-substituents. Presence of the substituent groups, regardless of the electronic properties, provided a marked bias toward the α′-methylene migration (Table 3). We would postulate that this regioselection relies primarily on a yet unreported controlling factor, chiral orientation of the hydroxyl group in the transient tetrahedral intermediate. *A priori* three types of transition states, **59**—**61**, are conceivable for the concerted fragmentation. The cyclic structures, however, can hardly explain the preference of R_m migration. The five-membered ring **59** is rather rigid and, when an oxabicyclic ketone is employed as starting material, this has basically C_s symmetry. The seven-membered structure **60** is more flexible but the fragmentation *via* such transition state is symmetry-forbidden in nature. On the other hand, the acyclic, extended transition state **61** has a chiral basic geometry; R_m and R_r are clearly diastereotopic each other and are to be differentiated during the concerted fragmentation process.[17] In order for R_m to migrate to O(1) atom with concomitant carboxylic acid ejection, two prerequisites must be satisfied. Firstly, R_m–C–O(1)–O(2) should lie in an antiperiplanar manner. Secondly, since the electron release from the hydroxyl oxygen to the migration origin attached to it is crucial to promote the shift of R_m,[18] one of the hydroxyl nonbonding electron pairs has to be anti to R_m. On the basis of such stereoelectronic requirements, only **61A** and **61B** are the reactive conformers. Conformer **61C** is unreactive. When this consideration is applied to the reaction of the oxabicyclic ketones **43**—**50**, four structures, **58A**, **58B**, **58A′**, and **58B′**, emerge as reactive conformers; **58A** and **58B** lead to the α-methylene migration product, whereas **58A′** and **58B′** result in α′-carbon rearrangement. Here when the nonbonded repulsion between R and the hydroxyl hydrogen is taken into consideration, the relative stabilities are estimated to be **58A′**>**58A**≫**58B**≈**58B′**, consistent with the observed α′-regioselection.[19] Thus chiral arrangement of the hydroxy group in the tetrahedral intermediate seems quite significant in controlling the regiochemical outcome. In this system, through-bond electronic effects of the γ substituents are less important compared with the above described series, because of the stereochemical arrangement is not appropriate for the transmission.[20]



59 **60** **61**



61A **61B** **61C**



58A **58B** **58A′** **58B′**

Experimental

General. All melting and boiling points are uncorrected. IR spectra were recorded on a JASCO IRA-1 spectrometer in $CHCl_3$ solution unless otherwise stated. ^1H NMR spectra were obtained using a Varian NV-21 or HA-100 spectrometer, and ^{13}C NMR spectra were recorded at 20 MHz on a Varian CFT-20 spectrometer or at 25 MHz on a JEOL FX-100 spectrometer. The chemical shifts are recorded in parts per million relative to tetramethylsilane as an internal standard. Singlet, doublet, triplet, and multiplet were abbreviated to s, d, t, and m, respectively. Low-resolution mass spectra were measured on a JEOL D 100 instrument and only a parent peak or prominent fragment peaks are described. Exact mass spectra were obtained at Center Research Laboratory of Ono Pharmaceutical Co. Elemental analyses were performed at the Research Laboratory of Fujisawa Pharmaceutical Co., Faculty of Engineering of Nagoya University, and Institute of Pharmaceutical Sciences of Meijo University. Drying of organic extracts was done over anhyd Na_2SO_4. For concentration of organic solvents, a vacuum (50—100 mmHg)** rotary evaporator was used. Bulb-to-bulb short-path distillation was performed by using a Büchi Kugelrohrofen. The cited temperatures for these distillations refer to the maximum temperature attained by the oven during the distillation and are thus not true boiling points.

Chromatography. Thin-layer chromatography (TLC) was done using 0.25-mm layers of silica gel 60 PF_{254} obtained from E. Merck and preparative TLC using 20×20-cm glass plates coated with a 1.0-mm layer of silica gel 60 PF_{254}. Analytical plates were visualized by spraying with a solution of 2% $Ce(SO_4)_2$ in 5% H_2SO_4 or 2% *p*-anisaldehyde in 5% ethanolic H_2SO_4 followed by heating on a hot plate. The position of spots is shown by R_f values. For column chromatography, E. Merck Kieselgel 60 (70—230 mesh) was used. High-performance liquid chromatography (HPLC) was performed with a Waters Model 6000A liquid chromatograph equipped with a Radial Pak B column (4.0ϕ×250) and a refractive index detector or a UV index detector. The position of peaks is shown by V_R (retention volume) values.

Solvents and Materials. DMF, pyridine, *t*-C_4H_9OH, and furan were used after distillation from CaH_2. Acetone and CH_2Cl_2 were distilled from P_2O_5. THF and ether were distilled from sodium benzophenone ketyl. CH_3OH was distilled over magnesium ribbons. Preparation of Zn/Ag couple,[21] Zn/Cu couple,[22] pyridinium *p*-toluenesulfonate,[23] polybromo ketones,[24] pyridinium chlorochromate,[25] trimethylsilyl triflate,[26] 3-pentylfuran,[27] 3-*t*-butylfuran,[28] 3-phenylfuran,[29] 2-phenylfuran,[30] trifluoromethanesulfonic anhydride,[31] *N*-methylmorpholine *N*-oxide monohydrate,[32] 8-oxabicyclo[3.2.1]oct-6-en-3-one,[21b] (1*S**, 2*R**, 5*S**)-2-methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one,[21b] and 2,2-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one[21b] was performed according to the known procedures. Other commercially supplied materials and solvents were used as received.

Preparation of 2-Pentylfuran.[33] To a solution of *n*-C_4H_9Li, prepared from THF (200 ml)*** and *n*-C_4H_9Li in hexane (1.5 mol dm^{-3} solution, 293 ml, 0.44 mol), was added furan (29.1 ml, 0.40 mol) at −10 °C under argon. After stirring for 6 h at the same temperature, 1-bromopentane (54.5 ml, 0.44 mol) was added to this mixture. The resulting mixture was stirred at 25 °C for 12 h and then poured into ice water (300 ml). The organic layer was separated and the aqueous layer was extracted with ether (150 ml×2). The combined extracts were dried and evaporated. The residue was distilled under reduced pressure (64—65 °C/40 mmHg) to give 2-pentylfuran (31.5 g, 57%). ^1H NMR ($CDCl_3$) δ 0.90 (t, J=6.2 Hz, 3H), 1.1—1.9 (m, 6H), 2.62 (t, J=7.0 Hz, 2H), 5.99 (m, 1H), 6.27 (m, 1H), 7.30 (m, 1H).

Preparation of 3-(Benzyloxymethyl)furan. To a mixture of $LiAlH_4$ (760 mg, 20 mmol) in THF (10 ml) was added ethyl 3-furoate (2.80 g, 20 mmol) in THF (5 ml) at 0 °C under argon. After stirring for 1 h at the same temperature, the reaction mixture was diluted with ether (15 ml). To this was added carefully 1 mol dm^{-3} NaOH (1 ml) and the insoluble material was removed by filtration. The filtrate was evaporated to give a colorless oil. To a suspension of NaH (50% oil dispersion, 1.25 g, 26 mmol) in DMF (10 ml) was added the oil in DMF (5 ml) at room temperature. After stirring for 1 h at 50 °C, the mixture was cooled to room temperature. To this was added benzyl chloride (4.62 ml, 40 mmol) and the reaction mixture was stirred for 12 h and poured into ice water (40 ml) and extracted with ether (50 ml×2, 30 ml×1). The ether layer was dried and evaporated to give an oil. Chromatography of this oil on a silica-gel column (10:1 hexane–ethyl acetate) afforded 3-(benzyloxymethyl)furan (3.86 g, 100%). R_f= 0.39 (4:1 hexane–ethyl acetate); ^1H NMR ($CDCl_3$) δ 4.42 (s, $C\underline{H}_2OCH_2C_6H_5$), 4.52 (s, $CH_2\underline{H}_2C_6H_5$), 6.44 (s, H_4), 7.32 (s, C_6H_5), 7.40 (s, H_2 and H_5).

Preparation of 3-(Tetrahydropyran-2-yloxymethyl)furan. A mixture of ethyl 3-furoate (28.0 g, 0.20 mol) and $LiAlH_4$ (7.60 g, 0.20 mol) in THF (300 ml) was stirred for 1 h at 0 °C under argon. To this was added slowly 1 mol dm^{-3} NaOH (20 ml) and the resulting white precipitate was filtered off. The filtrate was evaporated to afford a colorless oil. A solution of this oil, 3,4-dihydro-2*H*-pyran (23.7 ml, 0.26 mol), and pyridinium *p*-toluenesulfonate (5.0 g) in CH_2Cl_2 (150 ml) was stirred for 12 h at 20 °C under argon. The mixture was washed with brine (50 ml×3), dried ($MgSO_4$), and evaporated to give a colorless oil. Chromatography of this oil on a silica-gel column using a 3:1 hexane–ethyl acetate mixture to afford 3-(tetrahydropyran-2-yloxymethyl) furan (29.3 g, 80%) as a colorless oil. R_f=0.19 (3:1 hexane–ethyl acetate); ^1H NMR ($CDCl_3$) δ 1.1—2.2 (m, CH_2), 3.4—4.1 (m, $CH_2C\underline{H}_2O$), 4.41 (d, J=12.4 Hz, $C\underline{H}_aH_b$-OTHP), 4.65 (d, J=12.4 Hz, $CH_a\underline{H}_b$OTHP), 4.69 (m, $CH_2OC\underline{H}OCH_2$), 6.43 and 7.42 (m, H_1, H_2, and H_4).

Preparation of 8-Oxabicyclo[3.2.1]octan-3-one. A mixture of 8-oxabicyclo[3.2.1]oct-6-en-3-one (133 mg, 1.07 mmol), 10% Pd/C (20 mg), and ether (4 ml) was stirred for 16 h at 25 °C under hydrogen and the insoluble material was removed by filtration and the filtrate was evaporated to afford the title compound (129 mg, 95%). ^1H NMR ($CDCl_3$) δ 1.70—2.20 (m, H_6 and H_7), 2.32 (dd, J=1.0, 15.5 Hz, H_{2a} and H_{4a}), 2.77 (dd, J=5.0, 15.5 Hz, H_{2b} and H_{4b}), 4.75 (m, H_1 and H_5); ^{13}C NMR ($CDCl_3$) δ 29.66, 49.75, 74.84, 206.67.

Preparation of 8-Oxabicyclo[3.2.1]oct-6-en-3-one Derivatives. (1S,2R*,5S*)-2-Pentyl-8-oxabicyclo[3.2.1]oct-6-en-3-one*: To a mixture of Zn/Ag couple (68.7 g, 1.05 g-atom), furan (240 ml, 3.5 mol), and THF (600 ml) was added 1,1,3,3-tetrabromo-2-octanone (310 g, 0.7 mol) in THF (600 ml) over 1 h at −10 °C under argon. The reaction mixture was stirred at the same temperature for 1 h and then at 25 °C for 39 h. The insoluble material was filtered off and the filtrate was concentrated to dryness. The residue was dissolved in 1.2 l of CH_3OH saturated with NH_4Cl and to this was added Zn/Cu couple (240 g, 3.6 g-atom). The mixture was stirred for 1 h at 25 °C and the insoluble material

** 1 mmHg≈133.322 Pa.

*** 1 ml=0.001 dm^3.

was removed by filtration. The filtrate was diluted with H_2O (300 ml) and saturated disodium dihydrogen ethylenediaminetetraacetate (Na_2H_2edta) (300 ml) and then extracted with CH_2Cl_2 (500 ml×1, 200 ml×2), dried (Na_2SO_4), evaporated to afford a yellow oil. This oil was chromatographed on a silica-gel column using a 10:1 to 3:1 hexane–ethyl acetate mixture to give the title compound (63.2 g, 47%). Analytically pure sample was obtained by bulb-to-bulb distillation (130 °C/0.01 mmHg). R_f=0.31 (3:1 hexane–ethyl acetate); IR 1715 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.90 (t, J=6.0 Hz, CH_3), 1.30 (m, CH_2), 1.26 (d, J=5.0 Hz, H_{4a}), 1.70 (m, H_2), 1.74 (dd, J=5.0, 15.0 Hz, H_{4b}), 4.96 (d, J=5.0 Hz, H_1), 5.02 (d, J=5.0 Hz, H_5), 6.27 (s, H_6 and H_7); MS m/z 194 (M^+). Found: C, 74.32; H, 9.02%. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34%.

(1S,2S*,5S*)-2-Phenyl-8-oxabicyclo[3.2.1]oct-6-en-3-one*: A mixture of 1-phenyl-1,1,3,3-tetrabromo-2-propanone (90 g, 0.20 mol), Zn/Ag couple (19.5 g, 0.30 g-atom), furan (72.7 ml, 1.0 mol), and THF (250 ml) was stirred for 12 h at 25 °C. Reduction with Zn/Cu couple (65 g, 1.0 g-atom) in NH_4Cl/CH_3OH (700 ml) followed by ordinary extractive workup gave a dark oil. Chromatography of this oil on a silica-gel column using a 3:1 to 1:1 hexane–ethyl acetate mixture afforded 19.2 g (48%) of the title compound. Analytically pure sample was obtained by recrystallization from hexane. Mp 112.8—113.1 °C; R_f=0.35 (1:1 hexane–ethyl acetate); IR 1715 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.23 (dd, J=2.5, 16.4 Hz, H_{4a}), 2.88 (dd, J=4.7, 16.4 Hz, H_{4b}), 4.42 (d, J=4.9 Hz, H_2), 5.00 (dd, J=1.5, 4.9 Hz, H_1), 5.13 (ddd, J=1.5, 2.5, 4.7 Hz, H_5), 6.31 (dd, J=1.5, 7.0 Hz, H_6), 6.45 (dd, J=1.5, 7.0 Hz, H_7), 7.10 and 7.30 (m, C_6H_5); MS m/z 200 (M^+). Found: C, 78.05; H, 6.09%. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04%.

(1R,5S*)-1-Methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one*: A solution of $\alpha,\alpha,\alpha',\alpha'$-tetrabromoacetone (212 g, 0.60 mol) in THF (200 ml) was added to a mixture of Zn/Ag couple (39.0 g, 0.60 g-atom), 2-methylfuran (30.0 ml, 0.30 mol), and THF (200 ml) over 1 h at −10 °C. The resulting mixture was stirred for 1 h at the same temperature and then for 24 h at 25 °C. Reductive workup with Zn/Cu couple (130 g, 2.0 g-atom) in NH_4Cl/CH_3OH (400 ml) followed by ordinary extractive workup gave a brown oil. Purification of this oil by chromatography on a silica-gel column (4:1 hexane–ethyl acetate) afforded the title compound (25.0 g, 60%) as an oil. R_f=0.22 (4:1 hexane–ethyl acetate); IR (neat) 1718 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.50 (s, CH_3), 2.1—2.9 (m, H_2 and H_4), 5.06 (ddd, J=1.2, 1.8, 5.0 Hz, H_5), 6.05 (d, J=5.8 Hz, H_7), 6.20 (dd, J=1.8, 5.8 Hz, H_6); MS m/z 138 (M^+). Found: m/z 138.0682. Calcd for $C_8H_{10}O_2$: M, 138.0681.

(1R,5S*)-1-Pentyl-8-oxabicyclo[3.2.1]oct-6-en-3-one*: A mixture of $\alpha,\alpha,\alpha',\alpha'$-tetrabromoacetone (112 g, 0.30 mol), Zn/Ag couple (13.0 g, 0.20 g-atom), 2-pentylfuran (15.0 g, 0.10 mol), and THF (250 ml) was stirred for 12 h at 25 °C. Reduction with Zn/Cu couple (100 g, 1.54 g-atom) in NH_4Cl/CH_3OH (300 ml) followed by extractive workup gave a brown oil. This oil was purified on a silica-gel column (4:1 hexane–ethyl acetate) to afford the title compound (9.70 g, 50%) as an oil. R_f=0.37 (4:1 hexane–ethyl acetate); IR (neat) 1718 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.91 (t, J=6.5 Hz, CH_3), 1.1—1.9 (m, CH_2), 2.1—2.8 (m, H_2 and H_4), 5.06 (ddd, J=1.1, 1.9, 5.0 Hz, H_5), 6.05 (d, J=6.0 Hz, H_7), 6.19 (dd, J=1.9, 6.0 Hz, H_6); MS m/z 194 (M^+). Found: m/z 194.1328. Calcd for $C_{12}H_{18}O_2$: M, 194.1307.

(1R,5S*)-1-Phenyl-8-oxabicyclo[3.2.1]oct-6-en-3-one*: A mixture of $\alpha,\alpha,\alpha',\alpha'$-tetrabromoacetone (77.8 g, 0.208 mol), Zn/Ag couple (9.0 g, 0.139 g-atom), 2-phenylfuran (10 g, 69.4 mmol), and THF (170 ml) was stirred for 48 h at 25 °C. Reduction with Zn/Cu couple (70 g, 1.08 g-atom) in NH_4Cl/CH_3OH (200 ml) followed by ordinary extractive workup gave a brown oil. Purification of this oil on a silica-gel column using a 4:1 hexane–ethyl acetate mixture afforded the title compound (8.60 g, 62%). Mp 94—96 °C (hexane–chloroform); R_f=0.29 (4:1 hexane–ethyl acetate); IR (neat) 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.39 (dd, J=1.0, 16.0 Hz, H_{4a}), 2.82 (s, H_2), 2.83 (dd, J=5.0, 16.0 Hz, H_{4b}), 5.26 (dd, J=1.0, 5.0 Hz, H_5), 6.30 (s, H_6 and H_7), 7.42 (m, C_6H_5); MS m/z 200(M^+). Found: C, 78.24; H, 6.06%. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04%.

(1S,5S*)-1-Acetoxymethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one*: A mixture of $\alpha,\alpha,\alpha',\alpha'$-tetrabromoacetone (3.74 g, 10 mmol), Zn/Ag couple (981 mg, 15.0 mg-atom), furfuryl acetate (7.0 g, 50 mmol), and THF (35 ml) was stirred for 12 h at 20 °C and worked up in a usual manner to give a dark oil. Chromatography on a silica-gel column using a 7:1 to 3:1 hexane–ethyl acetate mixture afforded 1.73 g (52%) of (1*S**, 2*R**,4*S**,5*R**)-1-acetoxymethyl-2,4-dibromo-8-oxabicyclo-[3.2.1]oct-6-en-3-one as a yellow solid. Pure sample was obtained by recrystallization from hexane–ethyl acetate. Mp 115—116.5 °C; R_f=0.14 (7:1 hexane–ethyl acetate); IR 1745 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.18 (s, CH_3CO), 4.54 (d, J=13.5 Hz, H_aH_bCOC=O), 4.67 (d, J=13.5 Hz, $H_a\underline{H_b}COC$=O), 4.90 (d, J=4.5 Hz, H_4), 4.95 (s, H_2), 5.12 (dd, J=2.0, 4.5 Hz, H_5), 6.32 (d, J=6.5 Hz, H_7), 6.60 (dd, J=2.0, 6.5 Hz, H_6). Found: C, 33.95; H, 2.71; Br, 44.99%. Calcd for $C_{10}H_{10}O_4Br_2$: C, 33.93, H, 2.85; Br, 45.15%.

Treatment of this dibromo ketone (1.50 g, 4.44 mmol) with Zn/Cu couple (6.0 g, 92.3 mg-atom) in CH_3OH–CH_3COCH_3 (5:1, 30 ml) saturated with NH_4Cl at 20 °C for 1 h followed by extractive workup afforded the title compound (776 mg, 89%) as a yellow oil. Analytical sample was obtained by bulb-to-bulb distillation (bp 120 °C/0.01 mmHg). R_f=0.22 (2:1 hexane–ethyl acetate); IR 1722 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.12 (s, CH_3CO), 2.2—2.9 (m, H_2 and H_4), 4.34 (s, CH_2OC=O), 5.13 (m, H_5), 6.09 (d, J=6.0 Hz, H_7), 6.30 (dd, J=2.0, 6.0 Hz, H_6); ^{13}C NMR ($CDCl_3$) δ 45.07, 47.57, 65.25, 77.73, 84.83, 132.73, 134.54, 170.18, 204.00. Found: C, 61.10; H, 6.28%. Calcd for $C_{10}H_{12}O_4$: C, 61.24; H, 6.17%.

(1S,5S*)-1-Benzyloxymethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one*: A mixture of $\alpha,\alpha,\alpha',\alpha'$-tetrabromoacetone (113 g, 0.3 mol), Zn/Ag couple (13.0 g, 0.2 g-atom), 2-(benzyloxymethyl)-furan (18.0 g, 95.7 mmol), and THF (300 ml) was stirred for 48 h at 30 °C and worked up in a usual manner to give a dark oil. Treatment of this oil with Zn/Cu couple (98 g, 1.5 g-atom) in NH_4Cl/CH_3OH (250 ml) at 25 °C for 1 h followed by silica-gel column chromotography using a 3:1 hexane–ethyl acetate mixture to afford 8.17 g (35%) of the title compound as a yellow oil. R_f=0.50 (1:1 hexane–ethyl acetate); IR (neat) 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.1—2.9 (m, H_2 and H_4), 3.65 (s, $C\underline{H_2}OCH_2C_6H_5$), 4.62 (s, $C\underline{H_2}C_6H_5$), 6.08 (d, J=6.0 Hz, H_7), 6.23 (dd, J=2.0, 6.0 Hz, H_6), 7.33 (s, C_6H_5).

(1R,5R*,6S*)-6-Benzoyloxy-8-oxabicyclo[3.2.1]octan-3-one (37)*: To a solution of 8-oxabicyclo[3.2.1]oct-6-en-3-one (5.70 g, 50 mmol)[21b] in dry toluene (50 ml) was added diisobutylaluminium hydride in toluene (1.5 mol dm^{-3} solution, 44 ml, 65 mmol) at −78 °C under argon. After stirring for 3 h, the mixture was diluted with ether (50 ml) and to this was added slowly saturated NH_4Cl (10 ml). The mixture was warmed up to room temperature and stirred for 1 h. The insoluble material was removed by a Celite 545

pad and the filtrate was evaporated to give 8-oxabicyclo-[3.2.1]oct-6-en-3-ol (4.73 g, 82%) as a white semi-solid. This material was used in the next step without further purification. R_f=0.17 (1:1 hexane–ethyl acetate); IR (neat) 3380 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 1.6—2.5 (m, H_2 and H_4), 4.0 (m, H_3), 4.74 (m, H_1 and H_5), 6.10 and 6.44 (s, 28:72 ratio).

A mixture of this alcohol (4.30 g, 37.1 mmol), pyridinium *p*-toluenesulfonate (931 mg, 3.71 mmol), 3,4-dihydro-2*H*-pyran (4.06 ml, 44.5 mmol), and CH_2Cl_2 (30 ml) was stirred for 48 h at 20 °C. The mixture was washed with brine (30 ml), dried, and evaporated to give a dark oil. Chromatography of the residue on a silica-gel column using a 4:1 hexane–ethyl acetate mixture afforded 3-(tetrahydropyran-2-yloxy)-8-oxabicyclo[3.2.1]oct-6-ene (6.68 g, 86%) as a colorless oil. R_f=0.39 (4:1 hexane–ethyl acetate); ^1H NMR ($CDCl_3$) δ 1.4—2.4 (m, 10H), 3.5 (m, 1H), 4.0 (m, 2H), 4.7 (m, 3H), 6.22 (m, 2H).

To a solution of this THP ether (3.30 g, 15.7 mmol) in dry THF (10 ml) was added BH_3 in THF (1.0 mol dm^{-3} solution, 6.8 ml, 6.8 mmol) at 0 °C under argon. The mixture was stirred for 1.5 h at 20 °C and to this was added H_2O (1 ml). After stirring for 10 min, 3 mol dm^{-3} NaOH (2.5 ml, 7.5 mmol) and 30% H_2O_2 (2.24 ml, 20.4 mmol) were added. The mixture was stirred for 1 h at 50 °C, cooled to room temperature, and diluted with ether (20 ml). The organic layer was separated, washed with brine, dried, and evaporated to give a colorless oil. To this oil in pyridine (10 ml) was added benzoyl chloride (2.39 ml, 20.4 mmol) under argon. The mixture was stirred for 12 h at 20 °C and evaporated. The residue was diluted with ether (50 ml), washed with brine, neutralized with 1 mol dm^{-3} HCl, dried, and evaporated to give a yellow oil. Chromatography of this oil on a silica-gel column using a 3:1 hexane–ethyl acetate mixture afforded (1*S**,5*R**,6*S**)-6-benzoyloxy-3-(tetrahydropyran-2-yloxy)-8-oxabicyclo[3.2.1]-oct-6-ene (4.64 g, 89%) as a colorless oil. R_f=0.31 (2:1 hexane–ethyl acetate); IR 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.5—2.4 (m, 8H), 2.70—3.14 (m, 1H), 3.40—3.66 (m, 1H), 3.76—4.22 (m, 2H), 4.30—4.82 (m, 3H), 5.37 (m, 1H), 5.76 (dd, J=3.0, 7.1 Hz) and 5.93 (dd, J=2.2, 7.1 Hz) (total 1H), 7.30 and 8.06 (m, C_6H_5).

A mixture of this benzoate (4.60 g, 13.9 mmol), pyridinium *p*-toluenesulfonate (349 mg, 1.39 mmol), and CH_3OH (30 ml) was stirred for 20 h at 20 °C. The mixture was evaporated and the residue was diluted with ether (50 ml). The ether layer was washed with brine, dried, and evaporated to give a colorless oil. To a mixture of pyridinium chlorochromate (5.89 g, 27.8 mmol), sodium acetate (658 mg, 8.34 mmol), and CH_2Cl_2 (30 ml) was added the oil, obtained above, in CH_2Cl_2 (15 ml). The mixture was stirred for 2 h at 20 °C and diluted with hexane (20 ml). The insoluble material was removed by filtration and the filtrate was evaporated and chromatographed on a silica-gel column (1:1 hexane–ethyl acetate) to afford 2.20 g (58%) of **37** as a white solid. Mp 142—143 °C (hexane–chloroform); R_f=0.49 (1:2 hexane–ethyl acetate); IR 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.2—2.9 (m, H_2, H_4, and H_7), 4.75 (d-like, J=5.2 Hz, H_5), 4.92 (m, H_1), 5.29 (dd, J=4.7, 5.2 Hz, H_6), 7.30 and 8.04 (m, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 38.13, 46.26, 49.10, 74.69, 78.14, 80.18, 128.44, 129.69, 133.22, 133.57, 166.23, 204.86. Found: C, 68.45; H, 5.69%. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73%.

*(1*R*,5R*,6S*)-6-Benzyloxy-8-oxabicyclo[3.2.1]octan-3-one* (**33**): To a mixture of **37** (492 mg, 2 mmol), 1,2-bis(trimethylsiloxy)ethane (492 mg, 2.4 mmol), and dry CH_2Cl_2 (5 ml) was added trimethylsilyl triflate in CH_2Cl_2 (0.05 mol dm^{-3} solution, 4 ml, 0.2 mmol) at 0 °C under argon. The mixture was stirred for 30 min at 20 °C and to this was added pyridine (0.1 ml). The reaction mixture was washed with brine, dried, and evaporated to afford ethylene acetal of **37** (580 mg, 100%) as white crystals. Mp 92—93 °C; R_f=0.47 (1:1 hexane–ethyl acetate); IR 1718 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.70 (d-like, J=14.7 Hz, 1H), 1.95—2.23 (m, 4H), 2.80 (dd, J=7.8, 14.7 Hz, 1H), 3.92 (m, OCH_2CH_2O), 4.45 (m, H_5), 4.66 (m, H_1), 5.69 (dd, J=2.7, 7.3 Hz, H_6), 7.45 and 8.02 (m, C_6H_5).

A mixture of this ethylene acetal (2.03 g, 7 mmol), lithium hydroxide (40 mg), and CH_3OH (25 ml) was stirred for 48 h at 15 °C under argon. The mixture was evaporated and the residue was diluted with ether (50 ml). The organic layer was washed with saturated NH_4Cl (10 ml), brine, dried, and evaporated to give a yellow oil. To a suspension of NaH (50% oil dispersion, 323 mg, 6.72 mmol) in DMF (10 ml) was added the above obtained oil in DMF (5 ml). The mixture was stirred for 1 h at 50 °C under argon. After the mixture was cooled to 0 °C, benzyl chloride (1.19 ml, 10.3 mmol) was added. The reaction mixture was stirred for 12 h at 15 °C and evaporated. The residue was diluted with ether (20 ml) and the ether layer was washed with brine, dried, and evaporated to give a yellow oil. Chromatography of this oil on a silica-gel column using a 1:1 hexane–ethyl acetate mixture afforded a colorless oil (1.14 g, 80%). ^1H NMR ($CDCl_3$) δ 1.55—2.19 (m, 5H), 2.59 (dd, J=7.0, 12.7 Hz, 1H), 3.89 (m, OCH_2CH_2O), 4.41 (m, 1H), 4.49 (s, $C\underline{H}_2C_6H_5$), 4.61 (m, 1H), 7.34 (s, C_6H_5).

A mixture of this oil (1.14 g, 4.14 mmol), oxalic acid (100 mg), THF (10 ml), and H_2O (10 ml) was stirred for 8 h at 50 °C. The mixture was evaporated, extracted with chloroform (30 ml), washed with brine, dried, and concentrated to give 872 mg (91%) of **33** as a white solid. Mp 55—57 °C (ether–hexane); R_f=0.35 (1:1 hexane–ethyl acetate); IR (neat) 1719 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.02—2.80 (m, H_2, H_4, and H_7), 3.94 (dd, J=3.2, 6.0 Hz, H_6), 4.46 (s, $C\underline{H}_2C_6H_5$), 4.64 (d-like, J=5.0 Hz, H_5), 4.80 (m, H_1), 7.30 (s, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 38.50, 46.80, 49.24, 71.23, 74.71, 79.55, 82.36, 127.72, 128.45, 137.85, 205.66. Found: C, 72.13; H, 6.90%. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94%.

*(1*R*,5R*,6S*)-6-Hydroxy-8-oxabicyclo[3.2.1]octan-3-one*: A mixture of **37** (10.0 g, 40.7 mmol), lithium hydroxide (293 mg, 12.2 mmol), and dry CH_3OH (100 ml) was stirred for 15 h at 20 °C under argon. The mixture was evaporated and the residue was chromatographed on a silica-gel column using 3:1 hexane–ethyl acetate to pure ethyl acetate afforded 9.39 g (98%) of the title compound as a colorless oil. R_f=0.18 (3:1 ethyl acetate–hexane); IR (neat) 3380 (OH), 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.0—2.8 (m, H_2, H_4, and H_7), 3.15 (s, OH), 4.27 (dd, J=3.2, 6.0 Hz, H_6), 4.51 (d-like, J=6.0 Hz, H_5), 4.84 (m, H_1); ^{13}C NMR ($CDCl_3$) δ 41.27, 46.14, 49.47, 74.70, 75.45, 82.69, 206.09.

*(1*R*,5R*,6S*)-6-t-Butyldimethylsiloxy-8-oxabicyclo[3.2.1]-octan-3-one* (**34**): A mixture of **37** (2.00 g, 8.13 mmol), lithium hydroxide (60 mg, 2.5 mmol), and CH_3OH (10 ml) was stirred for 12 h at 20 °C. The reaction mixture was evaporated to dryness and coevaporated with benzene (5 ml × 3). To the residue in DMF (10 ml) were added *t*-butyldimethylsilyl chloride (1.83 g, 12.2 mmol) and imidazole (1.66 g, 24.4 mmol) in DMF (15 ml).[34] The mixture was stirred for 12 h at 20 °C and evaporated. The residue was diluted with ethyl acetate, washed with brine, dried, and evaporated to give a pale yellow oil. This oil was chromatographed on a silica-gel column using a 2:1 hexane–ethyl acetate mixture to afford 1.83 g (90%) of **34** as a colorless oil. R_f=

0.45 (2:1 hexane–ethyl acetate); IR (neat) 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.02 (s, t-$C_4H_9(C\underline{H}_3)_2Si$), 0.85 (s, t-$C_4\underline{H}_9(CH_3)_2Si$), 1.94—2.79 (m, H_2, H_4, and H_7), 4.20 (dd, J=3.8, 6.0 Hz, H_6), 4.41 (d-like, J=5.2 Hz, H_5), 4.80 (m, H_1); ^{13}C NMR ($CDCl_3$) δ 18.01, 25.78, 42.02, 46.78, 49.28, 74.93, 76.08, 83.02, 205.76.

(1R,5R*,6S*)-6-Acetoxy-8-oxabicyclo[3.2.1]octan-3-one (**35**)*: A mixture of (1*R**,5*R**,6*S**)-6-hydroxy-8-oxabicyclo[3.2.1]-octan-3-one (426 mg, 3 mmol), pyridine (2 ml), and acetic anhydride (2 ml) was stirred for 12 h at 20 °C under argon. The reaction mixture was evaporated and the residue was chromatographed on a silica-gel column using a 2:1 ethyl acetate–hexane mixture to afford 564 mg (100%) of **35** as a white solid. Mp 57—58 °C (hexane–chloroform); R_f= 0.40 (2:1 ethyl acetate–hexane); IR 1732 and 1723 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.07 (s, CH_3CO), 2.14—2.88 (m, H_2, H_4, and H_7), 4.62 (d-like, J=5.2 Hz, H_5), 4.88 (m, H_1), 5.06 (dd, J=4.7, 6.0 Hz, H_6); ^{13}C NMR ($CDCl_3$) δ 20.81, 38.02, 46.15, 49.05, 74.58, 77.32, 80.06, 170.40, 204.78. Found: C, 58.58; H, 6.63%. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57%.

(1R,5R*,6S*)-6-Pivaloyloxy-8-oxabicyclo[3.2.1]octan-3-one (**36**)*: To a solution of (1*R**,5*R**,6*S**)-6-hydroxy-8-oxabicyclo[3.2.1]octan-3-one (426 mg, 3 mmol) in dry pyridine (7 ml) was added pivaloyl chloride (0.75 ml, 6 mmol) at 0 °C under argon. After stirring for 12 h at 20 °C, the mixture was concentrated. The residue was chromatographed on a silica-gel column using a 1:1 hexane–ethyl acetate mixture to give **36** (687 mg, 100%) as a white solid. Mp 57—58 °C (ether–hexane); R_f=0.50 (1:1 hexane–ethyl acetate); IR 1723 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.19 (s, t-C_4H_9), 2.08—2.86 (m, H_2, H_4, and H_7), 4.55 (d-like, J=5.5 Hz, H_5), 4.86 (m, H_1), 5.01 (dd, J=4.0, 6.0 Hz, H_6); ^{13}C NMR ($CDCl_3$) δ 27.04, 38.02, 38.51, 46.32, 49.04, 74.64, 77.42, 80.14, 178.04, 204.77. Found: C, 63.40; H, 8.11%. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02%.

6-Methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one: To a mixture of Zn/Ag couple (39.0 g, 0.60 g-atom), 3-methylfuran (4.6 g, 0.3 mol), and THF (300 ml) was added a solution of $\alpha,\alpha,\alpha',\alpha'$-tetrabromoacetone (337 g, 0.9 mol) in THF (150 ml) over 1 h at 0 °C. After stirring for 14 h at 25 °C, the mixture was concentrated. Reduction with Zn/Cu couple (293 g, 4.5 g-atom) in NH_4Cl/CH_3OH (500 ml) followed by ordinary extractive workup afforded a brown oil. Chromatography of this oil on a silica-gel column using a 5:1 hexane–ethyl acetate mixture afforded the title compound (35.8 g, 86%) as an oil. R_f=0.26 (5:1 hexane–ethyl acetate); IR (neat) 1718 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.78 (s, CH_3), 2.16—2.82 (m, H_2 and H_4), 4.70 (d, J=5.0 Hz, H_5), 4.94 (m, H_1), 5.78 (m, H_7); ^{13}C NMR ($CDCl_3$) δ 11.75, 45.04, 45.44, 77.08, 79.94, 126.24, 142.96, 204.25; MS m/z 138 (M^+).

6-Pentyl-8-oxabicyclo[3.2.1]oct-6-en-3-one: A mixture of 3-pentylfuran (3.59 g, 26 mmol), Zn/Ag couple (3.36 g, 52 mg-atom), $\alpha,\alpha,\alpha',\alpha'$-tetrabromoacetone (29.2 g, 78 mmol), and THF (66 ml) was stirred for 48 h at 30 °C under argon. Reduction with Zn/Cu couple (26 g, 0.39 g-atom) in NH_4Cl/CH_3OH (100 ml) followed by ordinary extractive workup gave a brown oil. Purification of this oil on a silica gel column using a 6:1 hexane–ethyl acetate mixture afforded 984 mg (20%) of the title compound as an oil. R_f=0.43 (3:1 hexane–ethyl acetate); IR (neat) 1718 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.90 (m, CH_3), 1.1—1.7 (m, CH_2), 2.0—2.9 (m, CH_2, H_2, and H_4), 4.79 (d, J=4.8 Hz, H_5), 4.99 (m, H_1), 5.81 (m, H_7); ^{13}C NMR ($CDCl_3$) δ 13.96, 20.50, 27.22, 31.67, 46.37, 77.81, 79.46, 125.56, 148.81, 205.37.

6-t-Butyl-8-oxabicyclo[3.2.1]oct-6-en-3-one: A mixture of 3-t-butylfuran (9.18 g, 74 mmol), Zn/Ag couple (9.56 g, 148 mg-atom), $\alpha,\alpha,\alpha',\alpha'$-tetrabromoacetone (83.2 g, 222 mmol), and THF (177 ml) was stirred for 60 h at 20 °C under argon. Reduction with Zn/Cu couple (73 g, 1.11 g-atom) in NH_4Cl/CH_3OH (300 ml) followed by ordinary extractive workup gave a brown oil. Chromatography of this oil on a silica-gel column using a 5:1 to 1:1 hexane–ethyl acetate afforded the title compound (3.06 g, 23%) as an oil. R_f=0.50 (2:1 hexane–ethyl acetate); IR (neat) 1716 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.10 (s, t-C_4H_9), 2.1—3.0 (m, H_2 and H_4), 4.96 (m, H_1 and H_5), 5.82 (m, H_7); ^{13}C NMR ($CDCl_3$) δ 29.55, 31.73, 46.42, 48.13, 77.16, 77.56, 124.17, 128.34, 204.96.

6-Phenyl-8-oxabicyclo[3.2.1]oct-6-en-3-one: A mixture of 3-phenylfuran (5.51 g, 38.3 mmol), Zn/Ag couple (4.97 g, 76.6 mg-atom), $\alpha,\alpha,\alpha',\alpha'$-tetrabromoacetone (42.9 g, 115 mmol), and THF (100 ml) was stirred for 48 h at 19 °C. Reduction with Zn/Cu couple (49.8 g, 766 mg-atom) in NH_4Cl/CH_3OH (100 ml) followed by ordinary extractive workup afforded 1.69 g (22%) of the title compound as a solid. Mp 94.0—96.5 °C (ether–hexane); R_f=0.69 (2:1 ethyl acetate–hexane); IR 1715 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.3—3.0 (m, H_2 and H_4), 5.16 (m, H_1), 5.40 (m, H_5), 6.48 (d, J=2.2 Hz, H_7), 7.34 (s, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 45.87, 46.56, 77.97, 78.54, 125.90, 126.26, 128.85, 128.96, 131.45, 204.53.

6-(Tetrahydropyran-2-yloxymethyl)-8-oxabicyclo[3.2.1]oct-6-en-3-one: A mixture of 3-(tetrahydropyran-2-yloxymethyl)furan (17.0 g, 43.3 mmol), Zn/Ag couple (12.2 g, 0.187 g-atom), $\alpha,\alpha,\alpha',\alpha'$-tetrabromoacetone (105 g, 280 mmol), and THF (224 ml) was stirred for 60 h at 20 °C. Reduction with Zn/Cu couple (91 g, 1.4 g-atom) in NH_4Cl/CH_3OH (500 ml) followed by ordinary extractive workup gave the title compound (6.93 g, 31%) as a brown oil. R_f=0.44 (1:1 hexane–ethyl acetate); IR (neat) 1715 cm^{-1} (C=O), ^1H NMR ($CDCl_3$) δ 1.4—1.9 (m, 6H), 2.19—2.92 (m, H_2 and H_4), 3.32—3.95 (m, 2H), 4.14 (d, J=13.6 Hz, $\underline{H}_a\underline{H}_b$COTHP), 4.36 (d, J=13.6 Hz, $H_a\underline{H}_b$COTHP), 4.60 (br, OCHO), 4.98 (m, H_1 and H_5), 6.08 (m, H_7).

Preparation of 6,7-Isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one Derivatives. (1R,2R*,5S*,6S*,7R*)-6,7-Isopropylidenedioxy-2-methyl-8-oxabicyclo[3.2.1]octan-3-one (**1**)*: To a mixture of (1*S**,2*R**,5*S**)-2-methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (8.0 g, 57.9 mmol), acetone (60 ml), t-C_4H_9OH (6 ml), ether (6 ml), and OsO_4 (30 mg) was added 30% H_2O_2 (19.0 ml, 174 mmol) over 10 min at 0 °C. After stirring for 12 h at 25 °C, the mixture was cooled to 0 °C. To this was added slowly $Na_2S_2O_3\cdot5H_2O$ (30 g) and the reaction mixture was stirred for 3 h at 0 °C and concentrated. The residue was extracted with ethyl acetate (60 ml×4) and the organic extracts were dried and evaporated to give a dark solid. To a solution of this solid in acetone (100 ml) was added $CuSO_4$ (13 g) and p-toluenesulfonic acid (15 mg) and the mixture was stirred for 18 h at 25 °C. The insoluble material was removed by filtration and the filtrate was evaporated to give a yellow oil. Chromatography of this oil on a silica-gel column using a 2:1 to 1:1 hexane–ethyl acetate mixture afforded **1** (6.82 g, 56%). Mp 126.1—127.5 °C (ether); R_f=0.46 (1:1 hexane–ethyl acetate); IR 1710 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.28 (d, J=7.0 Hz, CH_3), 1.29 and 1.50 (s, isopropylidene CH_3), 2.34 (d, J=16.0 Hz, H_{4a}), 2.73 (dd, J=6.0, 16.0 Hz, H_{4b}), 2.80 (m, H_2), 4.39 (d, J=5.5 Hz, H_1), 4.46 (s, H_6 and H_7), 4.60 (d, J=6.0 Hz, H_5); MS m/z 197 (M^+—15). Found: C, 61.85; H, 7.72%. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60%.

(1R,2R*,5S*,6S*,7R*)-6,7-Isopropylidenedioxy-2-pentyl-8-oxabicyclo[3.2.1]octan-3-one (**2**)*: To a mixture of (1*S**,2*R**, 5*S**)-2-pentyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (26.8 g, 138

mmol), acetone (250 ml), ether (20 ml), t-C_4H_9OH (20 ml), and OsO_4 (200 mg) was added 30% H_2O_2 (75.9 ml, 691 mmol) over period of 1 h. After stirring for 24 h at 25 °C, OsO_4 (100 mg) and 30% H_2O_2 (50 ml) were further added. The mixture was stirred for 12 h and worked up in a usual manner to afford a pale green oil. This oil was dissolved in 150 ml of dry acetone and to this was added $CuSO_4$ (40 g) and p-toluenesulfonic acid (300 mg). The resulting mixture was stirred for 12 h at 25 °C and worked up in a usual manner to give a yellow oil. Chromatography of this oil on a silica-gel column using a 3:1 hexane–ethyl acetate mixture afforded 18.5 g (50%) of **2**. Analytically pure sample was obtained by bulb-to-bulb distillation (160 °C/0.03 mmHg). Mp 45—47 °C; R_f=0.54 (1:1 hexane–ethyl acetate); IR 1719 cm^{-1} (C=O); ^1H NMR (C_6D_6) δ 0.84 (t-like, J=6.0 Hz, CH_3), 1.09 and 1.51 (s, isopropylidene CH_3), 1.20 (m, CH_2), 1.83 (d, J=15.0 Hz, H_{4a}), 2.16 (dd, J=6.0, 15.0 Hz, H_{4b}), 2.20 (m, H_2), 4.08 (d, J=6.0 Hz, H_6), 4.27 (d, J=6.0 Hz, H_7), 4.40 (m, H_1 and H_5); MS m/z 253 (M^+−15). Found: C, 67.34; H, 9.01%. Calcd for $C_{15}H_{24}O_4$: C, 67.13; H, 9.02%.

(1S,5S*,6S*,7S*)-2,2-Dimethyl-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one (**4**)*: A mixture of 2,2-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (12.8 g, 84.2 mmol), acetone (240 ml), t-C_4H_9OH (24 ml), ether (24 ml), OsO_4 (100 mg), and 30% H_2O_2 (28 ml, 253 mmol) was stirred for 12 h at 25 °C and worked up in a usual manner to afford a white solid. To a solution of this solid in acetone (150 ml) was added $CuSO_4$ (20 g) and p-toluenesulfonic acid (100 mg) and the mixture was stirred for 12 h at 25 °C. Usual workup left a yellow oil. Chromatography of the residue on a silica-gel column using a 3:1 hexane–ethyl acetate mixture afforded **4** (11.2 g, 59%). Mp 109.5—110 °C (ether); R_f=0.34 (2:1 hexane–ethyl acetate); IR 1709 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.11 and 1.34 (s, CH_3), 1.31 and 1.50 (s, isopropylidene CH_3), 2.20 (d, J=16.0 Hz, H_{4a}), 2.91 (dd, J=6.0, 16.0 Hz, H_{4b}), 4.02 (s, H_1), 4.44 (d, J=5.5 Hz, H_6), 4.52 (d, J=6.0 Hz, H_5), 4.60 (d, J=5.5 Hz, H_7); MS m/z 226 (M^+). Found: C, 63.74; H, 8.07%. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02%.

(1R,2S*,5S*,6S*,7R*)-6,7-Isopropylidenedioxy-2-phenyl-8-oxabicyclo[3.2.1]octan-3-one (**3**)*: A mixture of (1*S**,2*S**,5*S**)-2-phenyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (5.10 g, 25.5 mmol), acetone (50 ml), ether (5 ml), t-C_4H_9OH (5 ml), and OsO_4 (30 mg) was added 30% H_2O_2 (7 ml, 63 mmol) at 0 °C. The resulting mixture was stirred for 24 h at 25 °C and worked up in a usual manner to give a yellow solid. To a solution of this solid in 30 ml of dry acetone was added $CuSO_4$ (5 g) and p-toluenesulfonic acid (10 mg) and the mixture was stirred for 20 h at 25 °C. Usual workup in a usual manner followed by purification on a silica-gel column using a 2:1 hexane–ethyl acetate mixture afforded **3** (3.55 g, 51%). Mp 162.3—162.8 °C (hexane–ethyl acetate); R_f=0.42 (1:1 hexane–ethyl acetate); IR 1710 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.28 and 1.50 (s, isopropylidene CH_3), 2.48 (d, J=16.0 Hz, H_{4a}), 2.88 (dd, J=6.0, 16.0 Hz, H_{4b}), 4.02 (d, J=5.0 Hz, H_2), 4.61 (d, J=5.7 Hz, H_6), 4.65 (m, H_1 and H_5), 4.78 (d, J=5.7 Hz, H_7); MS m/z 274 (M^+). Found: C, 70.17; H, 6.46%. Calcd for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61%.

(1R,5S*,6S*,7S*)-6,7-Isopropylidenedioxy-1-methyl-8-oxabicyclo[3.2.1]octan-3-one (**9**)*: To a solution of (1*R**,5*S**)-1-methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (25.0 g, 181 mmol), acetone (181 ml), t-C_4H_9OH (18 ml), ether (18 ml), and OsO_4 (400 mg) was added 30% H_2O_2 (39.3 ml, 362 mmol) and the resulting mixture was stirred for 12 h at 25 °C. The mixture was subjected to usual workup to give oily residue. A mixture of the resulting oil, $CuSO_4$ (50 g), p-toluenesulfonic acid (170 mg), and acetone (180 ml) was stirred for 12 h at 25 °C. The mixture was usually worked up to give a black oil, which was purified on a silica-gel column using a 5:1 to 3:1 hexane–ethyl acetate to afford **9** (20.3 g, 53%). Mp 76—77 °C (hexane–chloroform); R_f=0.40 (2:1 hexane–ethyl acetate); IR 1719 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.30 and 1.52 (s, isopropylidene CH_3), 1.42 (s, CH_3), 2.2—2.8 (m, H_2 and H_5), 4.30 (d, J=5.7 Hz, H_7), 4.51 (d, J=5.7 Hz, H_6), 4.55 (dd, J=1.8, 5.2 Hz, H_5); ^{13}C NMR ($CDCl_3$) δ 20.11, 24.99, 26.15, 45.12, 52.70, 78.99, 83.72, 84.45, 84.68, 112.39, 205.59; MS m/z 197 (M^+−15). Found: C, 61.97; H, 7.84%. Calcd for $C_{11}H_{16}O_4$: C, 62.25, H, 7.60%.

(1R,5S*,6S*,7S*)-6,7-Isopropylidenedioxy-1-pentyl-8-oxabicyclo[3.2.1]octan-3-one (**10**)*: A mixture of (1*R**,5*S**)-1-pentyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (9.70 g, 50.0 mmol), OsO_4 (100 mg), 30% H_2O_2 (11 ml, 100 mmol), acetone (150 ml), t-C_4H_9OH (15 ml), and ether (15 ml) was stirred for 24 h at 25 °C. The resulting mixture was worked up in a usual manner to produce a brown oil. A mixture of this oil, $CuSO_4$ (10 g), p-toluenesulfonic acid (100 mg), and acetone (100 ml) was stirred for 48 h at 25 °C and then worked up in a usual manner to give a brown oil. Chromatography of this oil using a 7:1 to 4:1 hexane–ethyl acetate mixture afforded **10** (7.0 g, 56%) as an oil. R_f=0.50 (4:1 hexane–ethyl acetate); IR 1719 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.91 (t, J=7.0 Hz, CH_3), 1.2—2.0 (m, CH_2), 1.29 and 1.50 (s, isopropylidene CH_3), 2.2—2.8 (m, H_2 and H_4), 4.33 (d, J=5.8 Hz, H_7), 4.49 (d, J=5.8 Hz, H_6), 4.55 (dd, J=1.7, 6.0 Hz, H_5); ^{13}C NMR ($CDCl_3$) δ 13.95, 22.55, 23.40, 25.05, 26.17, 32.39, 33.68, 45.52, 50.10, 78.88, 84.14, 84.44, 86.39, 112.29, 205.88; MS m/z 253 (M^+−15).

(1R,5S*,6S*,7S*)-6,7-Isopropylidenedioxy-1-phenyl-8-oxabicyclo[3.2.1]octan-3-one (**11**)*: A mixture of (1*R**,5*S**)-1-phenyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (14.7 g, 73.1 mmol), acetone (150 ml), t-C_4H_9OH (15 ml), ether (15 ml), OsO_4 (200 mg), and 30% H_2O_2 (16.2 ml, 146 mmol) was stirred at 25 °C. After stirring for 12 h, 30% H_2O_2 (8.1 ml, 73.1 mmol) was further added. After further stirring for 12 h, the reaction mixture was worked up in a usual manner to afford a black oil. A mixture of this oil, $CuSO_4$ (35 g), p-toluenesulfonic acid (200 mg), and acetone (100 ml) was stirred for 24 h at 25 °C and worked up in a usual manner to afford a brown solid. Chromatography of this solid using a silica-gel column (7:1 to 4:1 hexane–ethyl acetate) afforded **11** (10.1 g, 51%). Mp 166—168 °C (hexane–chloroform); R_f=0.48 (4:1 hexane–ethyl acetate); IR 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.24 and 1.34 (s, isopropylidene CH_3), 2.3—3.0 (m, H_2 and H_4), 4.61 (d, J=5.5 Hz, H_7), 4.69 (d, J=5.5 Hz, H_6), 4.77 (dd, J=1.5, 5.5 Hz, H_5), 7.2—7.6 (m, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 24.93, 26.00, 45.30, 53.01, 78.94, 84.48, 85.33, 87.48, 112.63, 125.51, 127.59, 128.26, 139.55, 205.50; MS m/z 259 (M^+−15). Found: C, 69.58, H, 6.76%. Calcd for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61%.

(1S,5S*,6S*,7S*)-1-Acetoxymethyl-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one (**17**)*: A mixture of (1*R**,5*S**)-1-acetoxymethyl-8-oxabicyclo[3.2.1]oct-6-en-one (13.1 g, 66.7 mmol), acetone (150 ml), t-C_4H_9OH (15 ml), ether (15 ml), OsO_4 (200 mg), and 30% H_2O_2 (14.7 ml, 133 mmol) was stirred for 20 h at 25 °C and worked up as usual. The residual oil was dissolved in acetone (150 ml) and to this was added $CuSO_4$ (20 g) and p-toluenesulfonic acid (100 mg). The resulting mixture was stirred for 12 h at 25 °C and worked up usual. Purification on a silica-gel column using a 3:1 to 1:1 hexane–ethyl mixture afforded 11.2 g

(62%) of **17** as a yellow oil. Analytically pure sample was obtained by recrystallization from hexane–chloroform. Mp 84—86 °C; R_f=0.40 (1:1 hexane–ethyl acetate); IR 1732 and 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.30 and 1.50 (s, isopropylidene CH_3), 2.12 (s, CH_3CO), 2.2—2.9 (m, H_2 and H_4), 4.36 (s, CH_2OC=O), 4.46 (d, J=6.0 Hz, H_7), 4.56 (d, J=6.0 Hz, H_6), 4.63 (m, H_5); ^{13}C NMR ($CDCl_3$) δ 20.44, 24.69, 25.85, 44.78, 47.57, 64.25, 79.45, 83.66, 84.01, 112.69, 170.02, 204.19. Found: C, 57.39; H, 6.66%. Calcd for $C_{13}H_{18}O_6$: C, 57.77; H, 6.71%.

(1S,5S*,6S*,7S*)-1-Benzyloxymethyl-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one (**16**)*: A mixture of (1*R**,5*S**)-1-benzyloxymethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (1.50 g, 6.14 mmol), acetone (20 ml), ether (2 ml), *t*-C_4H_9OH (2 ml), OsO_4 (30 mg), and 30% H_2O_2 (1.35 ml, 12.3 mmol) was stirred for 12 h at 25 °C. Usual workup left a brown oil, which was mixed with acetone (20 ml), $CuSO_4$ (5 g), and *p*-toluenesulfonic acid (10 mg), and kept for 12 h at 25 °C. Usual workup left a brown oil. Purification of this oil on a silica-gel column using a 4:1 hexane–ethyl acetate mixture afford **16** (1.07 g, 55%) as a yellow oil. R_f=0.23 (4:1 hexane–ethyl acetate); IR (neat) 1721 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.24 and 1.45 (s, isopropylidene CH_3), 2.1—3.0 (m, H_2 and H_4), 3.63 (d, J=11.0 Hz, $\underline{H}_a H_b COCH_2C_6H_5$), 3.78 (d, J=11.0 Hz, $H_a\underline{H}_bCOCH_2C_6H_5$), 4.40 (d, J=6.0 Hz, H_6), 4.50 (d, J=6.0 Hz, H_7), 4.58 (d, J=4.2 Hz, $\underline{H}_a H_b CC_6H_5$), 4.68 (d, J=4.2 Hz, $H_a\underline{H}_bCC_6H_5$), 4.72 (m, H_5), 7.33 (s, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 24.88, 26.04, 45.16, 48.13, 70.46, 73.71, 79.50, 84.03, 85.36, 112.52, 127.71, 128.39, 138.21, 205.41.

(1S,5S*,6S*,7S*)-1-Hydroxymethyl-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one*: A mixture of **17** (113 mg, 0.419 mmol) and lithium hydroxide (5 mg) in CH_3OH (2.5 ml) was stirred for 12 h at 20 °C under argon. The mixture was evaporated and the residue was triturated with CH_2Cl_2 (10 ml). Evaporation of the organic solvent afforded the title compound (96 mg, 96%) as a yellow oil. Analytically pure sample was obtained by recrystallization from ether–ethyl acetate–hexane. Mp 89—91 °C; R_f=0.31 (1:1 hexane–ethyl acetate); IR 3500 (OH), 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.28 and 1.50 (s, isopropylidene CH_3), 1.97 (br, OH), 2.2—2.9 (m, H_2 and H_4), 3.79 (d, J=11.5 Hz, $\underline{H}_a H_b COH$), 3.97 (d, J=11.5 Hz, $H_a\underline{H}_bCOH$), 4.47 (d, J=5.5 Hz, H_7), 4.56 (d, J=5.5 Hz, H_6), 4.62 (m, H_5). Found: C, 57.84; H, 7.07%. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07%.

(1S,5S*,6S*,7S*)-6,7-Isopropylidenedioxy-1-pivaloyloxymethyl-8-oxabicyclo[3.2.1]octan-3-one (**18**)*: To a mixture of (1*S**, 5*S**,6*S**,7*S**)-1-hydroxymethyl-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one (500 mg, 2.1 mmol) in pyridine (10 ml) was added pivaloyl chloride (0.52 ml, 4.1 mmol) at 0 °C under argon. The mixture was stirred for 30 min at the same temperature and for 12 h at 25 °C. The mixture was evaporated and the residue was partitioned between ethyl acetate and brine. The organic layer was dried and evaporated. The residue was chromatographed on a silica-gel column using a 4:1 hexane–ethyl acetate mixture to afford 639 mg (98%) of **18** as a colorless oil. Analytical sample was obtained by recrystallization from ether–hexane. Mp 88—90 °C, R_f=0.64 (1:1 hexane–ethyl acetate); IR 1724 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.24 (s, *t*-C_4H_9), 1.29 and 1.50 (s, isopropylidene CH_3), 2.2—2.9 (m, H_2 and H_4), 4.35 (s, CH_2OC=O), 4.45 (d, J=6.0 Hz, H_7), 4.55 (d, J=6.0 Hz, H_6), 4.63 (m, H_5); ^{13}C NMR ($CDCl_3$) δ 24.82, 25.98, 27.19, 38.89, 45.03, 47.87, 64.37, 79.57, 83.83, 84.07, 84.27, 112.78, 117.59, 204.44. Found: C, 61.54; H, 7.80%. Calcd for $C_{16}H_{24}O_6$: C, 61.52; H, 7.75%.

(1S,5S*,6S*,7S*)-1-Benzoyloxymethyl-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one (**19**)*: To a solution of (1*S**, 5*S**,6*S**,7*S**)-1-hydroxymethyl-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one (500 mg, 2.10 mmol) in pyridine (10 ml) was added benzoyl chloride (0.49 ml, 4.2 mmol) at 0 °C. The mixture was stirred for 30 min at 0 °C and then 12 h at 25 °C. The mixture was evaporated and the residue was diluted with benzene. The organic layer was washed with brine, 1 mol dm^{-3} HCl, saturated $NaHCO_3$, and then dried, and evaporated to give a yellow oil. Chromatography of this oil on a silica-gel column using a 3:1 hexane–ethyl acetate mixture afforded 615 mg (88%) of **19** as a white solid. Mp 152—153 °C (hexane–chloroform); R_f=0.55 (1:1 hexane–ethyl acetate); IR 1722 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.30 and 1.52 (s, isopropylidene CH_3), 2.2—2.9 (m, H_2 and H_4), 4.56 (s, CH_2OC=O), 4.62 (s, H_6 and H_7), 4.66 (m, H_5), 7.3—7.6 and 8.0—8.1 (m, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 24.93, 26.05, 45.09, 48.02, 64.86, 79.69, 83.90, 84.17, 113.01, 128.48, 129.74, 133.21, 204.49. Found: C, 64.76; H, 6.01%. Calcd for $C_{18}H_{20}O_6$: C, 65.05; H, 6.07%.

(1S,5S*,6S*,7S*)-6,7-Isopropylidenedioxy-1-trifluoroacetoxymethyl-8-oxabicyclo[3.2.1]octan-3-one (**20**)*: To a solution of (1*S**,5*S**,6*S**,7*S**)-1-hydroxymethyl-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one (100 mg, 0.420 mmol) in CH_2Cl_2 (2 ml) was added trifluoroacetic anhydride (135 μl, 0.840 mmol) at 0 °C. The mixture was stirred for 50 min at the same temperature and evaporated. Chromatography of the residue on a silica-gel column using a 4:1 hexane–ethyl acetate mixture afforded 103 mg (76%) of **20** as a colorless oil. Mp 84—85 °C (ether–hexane); R =0.57 (1:1 hexane–ethyl acetate); IR 1785 and 1725 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.28 and 1.50 (s, isopropylidene CH_3), 2.2—2.9 (m, H_2 and H_4), 4.4—4.8 (m, H_5, H_6, H_7, and H_2COC=O); ^{13}C NMR ($CDCl_3$) δ 24.65, 25.86, 44.80, 47.35, 67.64, 79.84, 83.41, 83.66, 84.19, 113.24, 158.04, 203.34. Found: C, 47.77; H, 4.80%. Calcd for $C_{13}H_{15}O_6F_3$: C, 48.15; H, 4.66%.

(1S,5S*,6S*,7S*)-6,7-Isopropylidenedioxy-1-mesyloxymethyl-8-oxabicyclo[3.2.1]octan-3-one (**21**)*: To a mixture of (1*S**, 5*S**,6*S**,7*S**)-1-hydroxymethyl-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one (500 mg, 2.1 mmol), triethylamine (0.59 ml, 4.2 mmol), and CH_2Cl_2 (10 ml) was added methanesulfonyl chloride (0.33 ml, 4.2 mmol). The mixture was stirred for 30 min at 0 °C and then 12 h at 28 °C. The mixture was diluted with CH_2Cl_2 (10 ml) and the organic layer was washed with brine, dried, and evaporated. Chromatography of the residue on a silica-gel column using a 1:1 hexane–ethyl acetate mixture afforded 635 mg (99%) of **21** as a white solid. Mp 149—151 °C (hexane–chloroform); R_f=0.31 (1:1 hexane–ethyl acetate); IR 1726 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.28 and 1.51 (s, isopropylidene CH_3), 2.2—2.9 (m, H_2 and H_4), 3.08 (s, CH_3), 4.4—4.7 (m, H_5, H_6, H_7, and CH_2OC=O); ^{13}C NMR ($CDCl_3$) δ 24.71, 25.98, 37.53, 44.85, 47.42, 69.57, 79.81, 83.60, 84.15, 113.13, 203.62. Found: C, 46.73; H, 5.74; S, 10.40%. Calcd for $C_{12}H_{18}O_7S$: C, 47.05; H, 5.92; S, 10.47%.

(1S,5S*,6S*,7S*)-1-t-Butyldimethylsiloxymethyl-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one (**15**)*: A mixture of (1*S**,5*S**,6*S**,7*S**)-1-hydroxymethyl-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one (500 mg, 2.10 mmol), *t*-butyldimethylsilyl chloride (479 mg, 3.15 mmol), and imidazole (428 mg, 6.30 mmol) in dry DMF (8 ml) was stirred for 12 h at 25 °C and then evaporated. The residue was partitioned between ethyl acetate and brine, and organic layer was separated, dried, and evaporated, leaving a colorless oil. Chromatography of this oil on a silica-gel column

using a 5:1 hexane–ethyl acetate mixture afforded 715 mg (100%) of **15** as a colorless oil. R_f=0.67 (1:1 hexane–ethyl acetate); IR (neat) 1724 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.08 (s, *t*-$C_4H_9(C\underline{H}_3)_2Si$), 0.92 (s, *t*-$C_4\underline{H}_9(CH_3)_2Si$), 1.28 and 1.50 (s, isopropylidene CH_3), 2.1—3.0 (m, H_2 and H_4), 3.86 (s, H_2COSi), 4.41 (d, J=5.7 Hz, H_7), 4.51 (d, J=5.7 Hz, H_6), 4.57 (m, H_5); ^{13}C NMR ($CDCl_3$) δ 18.35, 24.90, 25.92, 36.22, 45.31, 47.99, 63.94, 79.45, 83.68, 84.08, 86.09, 112.35, 205.85.

(1S,5S*,6S*,7S*)-6,7-Isopropylidenedioxy-1-trifluoromesyloxymethyl-8-oxabicyclo[3.2.1]octan-3-one (**22**)*: To a mixture of (1*S**,5*S**,6*S**,7*S**)-1-hydroxymethyl-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one (100 mg, 0.438 mmol), pyridine (70 μl, 0.876 mmol) in CH_2Cl_2 (3 ml) was added trifluoromethanesulfonic anhydride (111 μl, 0.657 mmol). The mixture was stirred for 15 min at 0 °C and diluted with CH_2Cl_2 (7 ml). To this was added saturated NaCl (1 ml) and the organic layer was dried and evaporated to give a yellow solid. Chromatography of this solid on a silica-gel column using a 2:1 hexane–ethyl acetate mixture afforded 138 mg (88%) of **22** as a white solid. Mp 103—104 °C (ether–hexane); R_f=0.65 (2:1 ethyl acetate–hexane); IR 1725 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.26 and 1.49 (s, isopropylidene CH_3), 2.22—2.91 (m, H_2 and H_4), 4.40—4.84 (m, H_5, H_6, H_7, and CH_2OSO_2); ^{13}C NMR ($CDCl_3$) δ 24.64, 25.81, 44.71, 47.03, 75.55, 80.81, 83.06, 83.60, 84.28, 113.50, 202.74. Found: C, 40.20; H, 4.33; S, 9.36%. Calcd for $C_{12}H_{15}O_7SF_3$: C, 40.00; H, 4.20; S, 8.90%.

(1S,5R*,6R*,7S*)-6,7-Isopropylidenedioxy-6-methyl-8-oxabicyclo[3.2.1]octan-3-one (**43**)*: *Method A.*[35] To a solution of 20% aqueous $(C_2H_5)_4NOH$ (0.59 ml, 0.80 mmol) and 6-methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (1.00 g, 7.25 mmol) in *t*-C_4H_9OH (13 ml) were added 70% *t*-C_4H_9OOH (2.24 ml, 17.4 mmol) and OsO_4 in *t*-C_4H_9OH (0.02 mol dm^{-3} solution, 3.62 ml, 0.0725 mmol) at 0 °C. After stirring for 1 h at 0 °C and for 12 h at room temperature, the mixture was cooled to 0 °C. To this were added renewedly 70% *t*-C_4H_9OOH (0.45 ml, 3.84 mmol) and OsO_4 in *t*-C_4H_9OH (0.02 mol dm^{-3} solution, 0.72 ml, 0.0144 mmol) and the mixture was further stirred for 24 h at room temperature. After the mixture was cooled to 0 °C, 20% aqueous $NaHSO_3$ (10 ml) was added. The mixture was stirred for 1 h and evaporated. The residue was dissolved in acetone (40 ml) and the insoluble material was removed by filtration. The filtrate was concentrated and the residue was dissolved in ethyl acetate (40 ml), dried, and evaporated to give a white solid. A mixture of this solid, $CuSO_4$ (3 g), *p*-toluenesulfonic acid (30 mg) and acetone (50 ml) was stirred for 1 h at room temperature. Usual workup left a pale yellow solid. Chromatography of this solid on a silica-gel column using a 3:1 to 1:1 hexane–ethyl acetate mixture afforded **43** (962 mg, 63%) as a white solid. Analytical sample was obtained by recrystallization from chloroform–hexane. Mp 72.0—73.0 °C; R_f=0.58 (1:1 hexane–ethyl acetate); IR 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.41 (s, CH_3), 1.41 and 1.50 (s, isopropylidene CH_3), 2.2—2.9 (m, H_2 and H_4), 4.15 (s, H_7), 4.45 (t-like, J=5.0 Hz, H_1 and H_5); ^{13}C NMR ($CDCl_3$) δ 21.09, 27.62, 28.26, 45.21, 45.39, 80.85, 83.23, 89.76, 91.17, 112.83, 204.86. Found: C, 62.28; H, 7.72%. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60%.

Method B.[32] To a solution of *N*-methylmorpholine *N*-oxide monohydrate (172 mg, 1.27 mmol) in H_2O (0.4 ml) and acetone (0.2 ml) were added a solution of OsO_4 in *t*-C_4H_9OH (0.02 mol dm^{-3} solution, 0.41 ml, 0.81×10^{-2} mmol) and 6-methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (138 mg, 1 mmol) at 20 °C. After stirring for 10 h, *N*-methylmorpholine *N*-oxide monohydrate (70 mg, 0.52 mmol) and OsO_4 in *t*-C_4H_9OH (0.02 mol dm^{-3} solution, 0.41 ml, 8.1×10^{-3} mmol) were added. The reaction mixture was stirred for an additional 12 h at 20 °C and to this was added a suspension of $Na_2S_2O_4$ (30 mg) and magnesol (300 mg) in H_2O (1.2 ml). After stirring for 10 min, the mixture was diluted with acetone (10 ml). The insoluble material was removed by filtration and the filtrate was evaporated. The residue was coevaporated with C_2H_5OH (10 ml×2). The crude material was dissolved in acetone (20 ml) and to this were added $CuSO_4$ (1.5 g) and *p*-toluenesulfonic acid (25 mg). The mixture was stirred for 2 h at 20 °C and worked up in a usual manner to give a yellow solid. Chromatography of this solid on a column of silica gel using a 3:1 hexane–ethyl acetate mixture afforded **43** (165 mg, 78%).

(1S,6R*,5R*,7S*)-6,7-Isopropylidenedioxy-6-pentyl-8-oxabicyclo[3.2.1]octan-3-one (**44**)*: To a solution of *N*-methylmorpholine *N*-oxide monohydrate (1.00 g, 7.14 mmol) in H_2O (2.0 ml) and acetone (1 ml) were added OsO_4 in *t*-C_4H_9OH (2.0×10^{-5} mol dm^{-3} solution, 2.38 ml, 47.6 μmol) and 6-pentyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (924 mg, 4.76 mmol). The mixture was stirred for 96 h at 15 °C and to this were added $Na_2S_2O_3\cdot5H_2O$ (242 mg) and magnesol (2.42 g) in H_2O (5 ml). Usual workup left a yellow oil. The mixture of this oil, dissolved in acetone (30 ml), $CuSO_4$ (2 g), and *p*-toluenesulfonic acid (500 mg) was stirred at 15 °C. After stirring for 1 h, *p*-toluenesulfonic acid (100 mg) was further added. The reaction mixture was stirred for 1 h and worked up in a usual way to afford a yellow solid. Chromatography of this solid on a silica-gel column using a 3:1 ethyl acetate–hexane mixture afforded **44** (718 mg, 56%). Mp 82—84 °C (hexane); R_f=0.84 (2:1 ethyl acetate–hexane); IR 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.89 (m, CH_3), 1.2—1.7 (m, CH_2), 1.41 and 1.53 (s, isopropylidene CH_3), 2.3—2.8 (m, H_2 and H_4), 4.14 (s, H_7), 4.50 (d-like, J=5.8 Hz, H_1 and H_5); ^{13}C NMR ($CDCl_3$) δ 13.88, 22.45, 24.31, 27.90, 28.68, 32.13, 34.45, 45.29, 45.78, 80.79, 82.44, 89.50, 94.77, 113.33, 205.07. Found: C, 66.95; H, 9.20%. Calcd for $C_{15}H_{24}O_4$: C, 67.13; H, 9.02%.

(1S,5R*,6R*,7S*)-6-t-Butyl-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one (**45**)*: To a solution of 6-*t*-butyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (1.00 g, 5.56 mmol) in THF (10 ml) was added OsO_4 (1.69 g, 6.65 mmol) in pyridine (7 ml). The mixture was stirred for 60 h at 30 °C in the dark and washed with ether (30 ml×3). The residue was dissolved in C_2H_5OH (10 ml) and H_2O (10 ml) and to this was added Na_2SO_3 (7.0 g). The mixture was heated at reflux for 6 h and the insoluble material was removed by filtration and the filtrate was evaporated to give a black solid. After this solid was coevaporated with C_2H_5OH, the residue was acetonized by standard method, as described above, to give 218 mg (15%) of **45**. Mp 121—123 °C (hexane–ether–ethyl acetate); R_f=0.71 (1:1 hexane–ethyl acetate); IR 1722 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.00 (s, *t*-C_4H_9), 1.46 and 1.62 (s, isopropylidene CH_3), 2.0—2.9 (m, H_2 and H_4), 4.38 (s, H_7), 4.3—4.6 (m, H_1 and H_5); ^{13}C NMR ($CDCl_3$) δ 27.79, 28.14, 34.68, 44.20, 46.13, 80.53, 82.41, 85.82, 100.97, 113.48, 204.66. Found: C, 66.04; H, 8.76%. Calcd for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72%.

(1S,5R*,6R*,7S*)-6,7-Isopropylidenedioxy-6-phenyl-8-oxabicyclo[3.2.1]octan-3-one (**46**)*: To a solution of *N*-methylmorpholine *N*-oxide monohydrate (1.69 g, 12.1 mmol) in H_2O (3.24 ml) and acetone (1.67 ml) were added OsO_4 in *t*-C_4H_9OH (2.0×10^{-5} mol dm^{-3} solution, 4.03 ml, 80.5 μ mol) and 6-phenyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (1.61 g, 8.05 mmol). After stirring for 72 h at 20 °C, *N*-methylmorpholine *N*-oxide monohydrate (0.56 g, 4.03 mmol) was further added. The mixture was further stirred for 72 h

and to this were added $Na_2S_2O_3 \cdot 5H_2O$ (410 mg) and magnesol (4.1 g) in H_2O. This mixture was worked up in a usual way to give a yellow solid. The solid was mixed acetone (40 ml) with $CuSO_4$ (5 g), and *p*-toluenesulfonic acid (0.2 g), and stirred at room temperature. After stirring for 1 h, *p*-toluenesulfonic acid (0.2 g) was further added. The resulting mixture was stirred for 3 h and worked up in a usual manner. Chromatography of the residue on a silica-gel column using a 4:1 to 1:1 hexane–ethyl acetate mixture afforded **46** (1.26 g, 57%). Mp 134—135 °C (hexane–ether–ethyl acetate); R_f=0.76 (2:1 ethyl acetate–hexane); IR 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.02 and 1.56 (s, isopropylidene CH_3), 1.7—3.0 (m, H_2 and H_4), 4.61 (d-like, J=6.5 Hz, H_1 and H_5), 4.92 (s, H_7), 7.34 (s, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 27.18, 36.29, 44.30, 45.45, 81.08, 83.31, 86.88, 95.92, 112.50, 126.14, 128.53, 128.83, 139.01, 204.54. Found: C, 69.77; H, 6.67%. Calcd for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61%.

(1S,5R*,6R*,7S*)-6-Hydroxymethyl-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one*: To a solution of *N*-methylmorpholine *N*-oxide monohydrate (4.41 g, 32.7 mmol) in H_2O (8.5 ml) and acetone (4.3 ml) was added OsO_4 in *t*-C_4H_9OH (0.02 mol dm^{-3} solution, 11.7 ml, 0.21 mmol). 6-(Tetrahydropyran-2-yloxymethyl)-8-oxabicyclo[3.2.1]oct-6-en-3-one (5.00 g, 21.0 mmol) was subjectedly added. The reaction mixture was stirred for 36 h at 20 °C and to this were added $Na_2S_2O_3$ (630 mg) and magnesol (6.3 g) in H_2O (25 ml). Usual workup left a yellow oil. A mixture of this oil, $CuSO_4$ (8 g), *p*-toluenesulfonic acid (300 mg), and acetone (50 ml) was stirred at the room temperature. After stirring for 3 h, *p*-toluenesulfonic acid (300 mg) was further added. The resulting mixture was stirred for 1 h and worked up in a usual way. Chromatography of the residue on a silica-gel column using a 4:1 to 1:1 hexane–ethyl acetate mixture afforded (1*S**,5*R**,6*R**,7*S**)-6,7-isopropylidenedioxy-6-(tetrahydropyran-2-yloxymethyl)-8-oxabicyclo[3.2.1]octan-3-one (1.07 g, 16%), mp 126—130 °C (ether–hexane); R_f=0.68 (2:1 ethyl acetate–hexane); IR 1721 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.42 and 1.54 (s, isopropylidene CH_3), 1.62 (m, 6H), 2.2—2.9 (m, H_2 and H_4), 3.3—4.1 (m, CH_2O), 4.3—4.7 (m, H_1, H_5, H_7, and OCHO). Found: C, 61.40; H, 7.87%. Calcd for $C_{16}H_{24}O_6$: C, 61.52; H, 7.75%, and the title compound (1.92 g, 40%). Mp 138—140 °C; R_f=0.35 (2:1 ethyl acetate–hexane); IR 3590 (OH), 1721 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.40 and 1.52 (s, isopropylidene CH_3), 2.2—2.9 (m, H_2 and H_4), 3.65 (d, J=12.0 Hz, $\underline{H}_aH_bCOH$), 3.85 (d, J=12.0 Hz, $H_a\underline{H}_bCOH$), 4.24 (s, H_7), 4.58 (m, H_1 and H_5); ^{13}C NMR ($CDCl_3$) δ 27.77, 28.57, 44.90, 45.27, 63.90, 80.87, 81.82, 86.60, 95.20, 114.07, 205.11. Found: C, 58.04; H, 7.22%. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07%.

Deprotection of (1S,5R*,6R*,7S*)-6,7-Isopropylidenedioxy-6-(tetrahydropyran-2-yloxymethyl)-8-oxabicyclo[3,2,1]octan-3-one.* A mixture of (1*S**, 5*R**, 6*R**,7*S*)-6,7-isopropylidenedioxy-6-(tetrahydropyran-2-yloxymethyl)-8-oxabicyclo[3.2.1]octan-3-one (6.13 g, 19.6 mmol) and oxalic acid dihydrate (819 mg, 6.5 mmol) in THF (19.6 ml) and H_2O (6 ml) was stirred at 50 °C. After stirring for 2 h, oxalic acid dihydrate (819 mg, 6.5 mmol) in H_2O (5 ml) was further added. After stirring for 4 h, the reaction mixture was evaporated. The residue was extracted with chloroform (40 ml×4) and the organic layer was dried and evaporated to give a yellow solid which was washed with ether. (1*S**,5*R**,6*R**,7*S**)-6-Hydroxymethyl-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]-octan-3-one was obtained as a white solid, 3.50 g (78%). The mother liquid was concentrated and the residue was chromatographed to afford the same compound (0.18 g, 4%). Total amount was 3.68 g (82%).

(1S,5R*,6R*,7S*)-6-t-Butyldimethylsiloxymethyl-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one (47)*: To a solution of (1*S**,5*R**,6*R**,7*S**)-6-hydroxymethyl-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one (1.86 g, 8.16 mmol) in dry DMF (25 ml) was added a solution of *t*-butyldimethylsilyl chloride (1.88 g, 12.5 mmol) and imidazole (1.70 g, 25 mmol) in dry DMF (25 ml).[34] The mixture was stirred for 30 min at 0 °C and for 20 h at 20 °C. The reaction mixture was evaporated and the residue was diluted with ether (250 ml). The organic layer was washed with brine, dried, and evaporated. The residual oil was chromatographed on a silica-gel column using a 4:1 hexane–ethyl acetate mixture to afford **47** (2.52 g, 90%) as a colorless oil. R_f=0.50 (3:1 hexane–ethyl acetate); IR (neat) 1725 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.08 (s, *t*-$C_4H_9(C\underline{H}_3)_2Si$) 0.90 (s, *t*-$C_4\underline{H}_9(CH_3)_2Si$), 1.40 and 1.52 (s, isopropylidene CH_3), 2.2—2.9 (m, H_2 and H_4), 3.66 (d, J=11.5 Hz, $\underline{H}_aH_bCOSi$), 3.86 (d, J=11.5 Hz, $H_a\underline{H}_bCOSi$), 4.24 (s, H_7), 4.50 (m, H_1 and H_5); ^{13}C NMR ($CDCl_3$) δ 18.41, 25.93, 27.87, 28.42, 44.53, 45.01, 65.10, 80.85, 82.08, 86.40, 95.15, 113.76, 204.60.

(1S,5R*,6R*,7S*)-6-Benzyloxymethyl-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one (48)*: To a solution of *N*-methylmorpholine *N*-oxide monohydrate (210 mg, 1.5 mmol) in H_2O (0.4 ml) and acetone (0.2 ml) were added OsO_4 in *t*-C_4H_9OH (2.0×10^{-5} mol dm^{-3} solution, 0.5 ml, 0.01 mmol) and 6-benzyloxymethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (244 mg, 1 mmol). The reaction mixture was stirred for 84 h at 20 °C and to this were added $Na_2S_2O_3$ (31 mg) and magnesol (310 mg) in H_2O (1.2 ml). Usual workup left a yellow oil. The mixture of this oil, dissolved in acetone (20 ml), $CuSO_4$ (1.5 g), and *p*-toluenesulfonic acid (50 mg) was stirred at 20 °C. After stirring for 30 min, *p*-toluenesulfonic acid (50 mg) was further added. The mixture was stirred for 2 h and worked up in a usual way. The residue was purified on a silica-gel column using a 4:1 hexane–ethyl acetate mixture to afford **48** (206 mg, 65%). Mp 90.5—91.5 °C (hexane–ethyl acetate); R_f=0.71 (2:1 ethyl acetate–hexane); ^1H NMR ($CDCl_3$) δ 1.34 and 1.50 (s, isopropylidene CH_3), 2.2—2.8 (m, H_2 and H_4), 3.48 (d, J=10.5 Hz, $\underline{H}_aH_bCOCH_2C_6H_5$), 3.66 (d, J=10.5 Hz, $H_a\underline{H}_bCOCH_2C_6H_5$), 4.26 (s, H_7), 4.4—4.6 (m, H_1 and H_5), 4.54 (s, $C\underline{H}_2C_6H_5$), 7.32 (s, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 27.82, 28.30, 44.72, 45.01, 71.33, 73.85, 80.73, 82.09, 86.88, 93.98, 114.05, 127.99, 128.52, 137.50, 204.56. Found: C, 68.19; H, 7.20%. Calcd for $C_{18}H_{22}O_5$: C, 67.91; H, 6.97%.

(1S,5R*,6R*,7S*)-6,7-Isopropylidenedioxy-6-pivaloyloxymethyl-8-oxabicyclo[3.2.1]octan-3-one (49)*: To a solution of (1*S**,5*R**,6*R**,7*S**)-6-hydroxymethyl-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one (456 mg, 2.00 mmol) in pyridine (10 ml) was added pivaloyl chloride (0.5 ml, 4.0 mmol) at 0 °C. The mixture was stirred for 30 min at 0 °C and for 12 h at 20 °C. After the mixture was evaporated, the residue was dissolved in ethyl acetate (50 ml). The ethyl acetate layer was washed with brine, dried, and evaporated. Chromatography of the residue on a silica-gel column using a 4:1 hexane–ethyl acetate mixture afforded 468 mg (75%) of **49**. Mp 97.0—98.5 °C (hexane–ether); R_f=0.55 (1:1 hexane–ethyl acetate); IR 1730 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.20 (s, *t*-C_4H_9), 1.40 and 1.51 (s, isopropylidene CH_3), 2.40 (dd, J=6.4, 17.0 Hz, H_{4a}), 2.76 (dd, J=3.0, 17.0 Hz, H_{4b}), 3.94 (d, J=12.5 Hz, $\underline{H}_aH_bCOC$=O), 4.38 (s, H_7), 4.54 (d, J=12.5 Hz, $H_a\underline{H}_bCOC$=O), 4.45—4.55 (m, H_1 and H_5); ^{13}C NMR ($CDCl_3$) δ 27.22, 27.77, 28.27, 39.00, 44.92, 45.53, 65.13, 81.09, 81.93, 86.43, 93.20, 114.39, 177.80, 204.23. Found: C, 61.22; H, 7.70%. Calcd

for $C_{16}H_{24}O_6$: C, 61.52; H, 7.75%.

(1S,5R*,6R*,7S*)-6-Benzoyloxymethyl-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one (**50**)*: To a solution of (1*S**, 5*R**,6*R**,7*S**)-6-hydroxymethyl-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one (456 mg, 2.0 mmol) in pyridine (10 ml) was added benzoyl chloride (0.47 ml, 4.0 mmol) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and for 12 h at 20 °C and evaporated. The residue was dissolved in benzene (10 ml) and washed with brine, 1 mol dm^{-3} HCl, saturated $NaHCO_3$, dried, and the benzene layer was evaporated. The residue was purified on a silica-gel column using a 3:1 hexane–ethyl acetate mixture to afford **50** (586 mg, 88%). Mp 164—168 °C (hexane–ether–ethyl acetate); R_f=0.59 (1:1 hexane–ethyl acetate); IR 1728 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.41 and 1.54 (s, isopropylidene CH_3), 2.3—3.0 (m, H_2 and H_4), 4.35 (d, J=12.2 Hz, $\underline{H}_a H_b COC{=}O$), 4.44 (s, H_7), 4.5—4.8 (m, H_1 and H_5), 4.70 (d, J=12.2 Hz, $H_a \underline{H}_b COC{=}O$), 7.3—7.8 (m, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 27.82, 28.32, 45.00, 45.59, 65.33, 81.22, 81.97, 86.86, 93.21, 114.68, 128.58, 128.97, 129.90, 130.67, 133.36, 134.51, 166.03, 204.20. Found: C, 65.18; H, 5.79%. Calcd for $C_{18}H_{20}O_6$: C, 65.05; H, 6.07%.

*Baeyer-Villiger Oxidation of α-Substituted Ketones. Oxidation of **1***: A mixture of **1** (6.80 g, 32.1 mmol) and Na_2HPO_4 (82.4 g, 580 mmol) in CH_2Cl_2 (100 ml) was cooled in an ice bath and stirred magnetically. To this was added dropwise over 15 min trifluoroperacetic acid, which had been prepared from 90% H_2O_2 (3.70 ml, 96.3 mmol) and trifluoroacetic anhydride (16.4 ml, 116 mmol) in CH_2Cl_2 (50 ml). The reaction mixture was stirred for 16 h at 25 °C under argon and to this was added $NaHSO_3$ (79 g) and $NaHCO_3$ (15 g). After stirring for 1 h, the insoluble material was removed by filtration. The filtrate was evaporated and the resulting yellow residue was chromatographed on a silica-gel column using a 1:1 to 1:2 hexane–ethyl acetate mixture to afford (1*R**,2*R**,6*S**,7*S**,8*R**)-7,8-isopropylidenedioxy-2-methyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**5**) (6.20 g, 85%). Mp 126.2—127.8 °C(chloroform–hexane); R_f= 0.34 (2:1 hexane–ethyl acetate); IR 1732 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.26 and 1.42 (s, isopropylidene CH_3), 1.31 (d, J=7.0 Hz, CH_3), 2.92 (m, H_5), 4.14 (s, H_1), 4.28 (t-like, J=4.0 Hz, H_6), 4.58 (q, J=7.0 Hz, H_2), 4.61 (d, J=6.0 Hz, H_7), 4.87 (d, J=6.0 Hz, H_8); MS *m/z* 213 (M^+—15). Found: C, 57.82; H, 6.91%. Calcd for $C_{11}H_{16}O_5$: C, 57.88, H, 7.07%.

*Oxidation of **2***: To a mixture of **2** (12.0 g, 44.7 mmol), Na_2HPO_4 (115 g, 0.807 mol), and CH_2Cl_2 (150 ml) was added slowly trifluoroperacetic acid in CH_2Cl_2 (1.53 mol dm^{-3} solution, 146 ml, 0.224 mol) under argon. After stirring for 8 h at 25 °C, solid $NaHCO_3$ (50 g) was added to the mixture. Usual workup left an oil, chromatography of which on a silica-gel column using a 5:1 hexane–ethyl acetate mixture afforded (1*R**,2*R**,6*S**,7*S**,8*R**)-7,8-isopropylidenedioxy-2-pentyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**6**) (9.80 g, 78%). Mp 64—65 °C (hexane); R_f=0.24 (3:1 hexane–ethyl acetate); IR 1732 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J=6.0 Hz, CH_3), 1.30 and 1.49 (s, isopropylidene CH_3), 1.50 (m, CH_2), 2.90 (dd, J=4.5, 16.5 Hz, H_{5a}), 3.07 (dd, J=3.0, 16.5 Hz, H_{5b}), 4.26 (s, H_1), 4.40 (m, H_6 and H_2), 4.65 (d, J=5.8 Hz, H_7), 4.93 (d, J= 5.8 Hz, H_8); MS *m/z* 269 (M^+—15). Found: C, 63.07; H, 8.67%. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51%.

*Oxidation of **3***: Trifluoroperacetic acid in CH_2Cl_2 (1.37 mol dm^{-3} solution, 28 ml, 38.3 mmol) was added slowly to a mixture of **3** (3.50 g, 12.7 mmol), Na_2HPO_4 (19.6 g, 138 mmol), and CH_2Cl_2 (30 ml) at 0 °C. After stirring for 11 h at 25 °C, solid $NaHCO_3$ (10 g) and $NaHSO_3$ (6 g) were added. The mixture was worked up in a usual manner to give a solid. Purification of this solid on a silica-gel column using a 2:1 to 1:1 hexane–ethyl acetate mixture afforded (1*S**,2*S**,6*S**,7*S**,8*S**)-7,8-isopropylidenedioxy-2-phenyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**7**) (2.45 g, 67%). Mp 160.8—161.2 °C (ether); R_f=0.30 (1:1 hexane–ethyl acetate); IR 1739 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.31 and 1.46 (s, isopropylidene CH_3); 3.00 (dd, J=2.5, 16.0 Hz, H_{5a}), 3.20 (dd, J=4.5, 16.0 Hz, H_{5b}), 4.41 (dd, J= 2.5, 4.5 Hz, H_6), 4.50 (s, H_1), 4.77 (d, J=6.0 Hz, H_7), 5.07 (d, J=6.0 Hz, H_8), 5.57 (s, H_2), 7.42 (br s, C_6H_5); MS *m/z* 290 (M^+). Found: C, 65.98; H, 6.23%. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25%.

*Oxidation of **4***: To a mixture of **4** (11.2 g, 49.6 mmol), Na_2HPO_4 (127 g, 0.895 mol), and CH_2Cl_2 (150 ml) was added trifluoroperacetic acid in CH_2Cl_2 (1.14 mol dm^{-3} solution, 131 ml, 149 mmol) at 0 °C. After stirring for 6 h at 25 °C, solid $NaHCO_3$ (15 g) and $NaHSO_3$ (7 g) were added. Usual workup left a yellow oil. Chromatography of the residue on a silica-gel column using a 2:1 hexane–ethyl acetate mixture afforded (1*S**,6*S**,7*S**,8*S**)-2,2-dimethyl-7,8-isopropylidenedioxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**8**) (9.70 g, 81%). Mp 158.5—159.2 °C (ether); R_f=0.35 (2:1 hexane–ethyl acetate); IR 1730 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.34 and 1.56 (s, isopropylidene CH_3), 1.46 and 1.50 (s, CH_3), 2.88 (dd, J=3.0, 17.0 Hz, H_{5a}), 3.12 (dd, J=4.0, 17.0 Hz, H_{5b}), 4.10 (s, H_1), 4.33 (dd, J=3.0, 4.0 Hz, H_6), 4.64 (d, J=6.0 Hz, H_7), 4.97 (d, J=6.0 Hz, H_8); MS *m/z* 227 (M^+—15). Found: C, 59.20; H, 7.46%. Calcd for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49%.

*The Baeyer-Villiger Oxidation of β-Substituted Ketones. Oxidation of **9***: To a mixture of **9** (9.35 g, 44.1 mmol), Na_2HPO_4 (61.8 g, 0.435 mol), Na_2H_2edta (3 g), and CH_2Cl_2 (150 ml) was added trifluoroperacetic acid in CH_2Cl_2 (1.74 mol dm^{-3} solution, 76 ml, 132 mmol) at 0 °C. The mixture was stirred for 10 h at 20 °C and usual workup left a white solid. ^{1}H NMR analysis of this material indicated that (1*R**,6*S**,7*S**,8*S**)-7,8-isopropylidenedioxy-1-methyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**12a**) and (1*S**,6*R**,7*S**,8*S**)-7,8-isopropylidenedioxy-6-methyl-3,9-dioxabicyclo[4.2.1]-nonan-4-one (**12b**) were produced in 53:47 ratio. Chromatography of this solid on a silica-gel column using a 3:1 ether–petroleum ether mixture afforded **12a** (5.5 g, containing 15% of **12b** determined by ^{1}H NMR) and **12b** (4.0 g, containing 10% of **12a** determined by ^{1}H NMR). Total yield was 90% (9.5 g). Pure samples of **12a** and **12b** were obtained by rechromatography and recrystallization from chloroform–hexane. **12a**: Mp 100—102 °C; R_f=0.35 (2:1 ether–petroleum ether); IR 1735 cm^{-1} (C=O); ^{1}H NMR (C_6D_6) δ 1.01 (s, CH_3), 1.07 and 1.40 (s, isopropylidene CH_3), 2.25 (dd, J=2.9, 15.5 Hz, H_{5a}), 2.45 (dd, J=4.1, 15.5 Hz, H_{5b}), 3.38 (d, J=14.0 Hz, H_{2a}), 3.56 (d, J=14.0 Hz, H_{2b}), 3.93 (dd, J=2.9, 4.1 Hz, H_6), 4.41 (d, J=6.0 Hz, H_7), 4.48 (d, J=6.0 Hz, H_8); MS *m/z* 213 (M^+—15). Found: C, 57.30; H, 7.05%. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07%. **12b**: Mp 100—101 °C; R_f=0.30 (2:1 ether–petroleum ether); IR 1735 cm^{-1} (C=O); ^{1}H NMR (C_6D_6) δ 1.05 and 1.38 (s, isopropylidene CH_3), 1.16 (s, CH_3), 2.34 (d, J=16.0 Hz, H_{5a}), 2.54 (d, J=16.0 Hz, H_{5b}), 3.36 (dd, J=4.0, 13.8 Hz, H_{2a}), 3.60 (d, J=13.8 Hz, H_{2b}), 3.91 (d, J=4.0 Hz, H_1), 4.33 (d, J=6.0 Hz, H_7), 4.67 (d, J=6.0 Hz, H_8); MS *m/z* 228 (M^+). Found: C, 57.90; H, 7.12%. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07%.

*Oxidation of **10***: Trifluoroperacetic acid in CH_2Cl_2 (1.54 mol dm^{-3} solution, 14.2 ml, 21.8 mmol) was added to a mixture of **10** (835 mg, 3.12 mmol), Na_2HPO_4 (10.2 g, 72.0

mmol), Na_2H_2edta (500 mg), and CH_2Cl_2 (20 ml) at 0 °C. The mixture was stirred for 15 h at 20 °C and the usual workup gave a white solid. ^1H NMR analysis of this solid indicated that (1*R**,6*S**,7*S**,8*S**)-7,8-isopropylidenedioxy-1-pentyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**13a**) and (1*S**,6*R**,7*S**,8*S**)-7,8-isopropylidenedioxy-6-pentyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**13b**) were produced in 50:50 ratio. Chromatographic separation (silica gel, 1:1 ether–petroleum ether) yielded 400 mg (45%) of **13a** and 406 mg (46%) of **13b**. Total yield was 91% (806 mg). **13a**: Mp 60—61 °C (chloroform–hexane); R_f=0.46 (2:1 ether–petroleum ether); IR 1734 cm^{-1} (C=O); ^1H NMR (C_6D_6) δ 0.85 (t, J=6.0 Hz, CH_3), 1.0—1.8 (m, CH_2), 1.07 and 1.42 (s, isopropylidene CH_3), 2.40 (m, H_5), 3.67 (s, H_2), 3.99 (dd, J=3.0, 4.7 Hz, H_6), 4.51 (s, H_7 and H_8); MS *m/z* 284 (M^+). Found: C, 63.19; H, 8.71%. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51%. **13b**: Mp 106—107 °C (chloroform–hexane); R_f=0.38 (2:1 ether–petroleum ether); IR 1735 cm^{-1} (C=O); ^1H NMR (C_6D_6) δ 0.86 (t, J=6.0 Hz, CH_3), 1.07 and 1.40 (s, isopropylidene CH_3), 1.2—1.9 (m, CH_2), 2.41 (d, J=15.5 Hz, H_{5a}), 2.72 (d, J=15.5 Hz, H_{5b}), 3.43 (dd, J=4.1, 13.2 Hz, H_{2a}), 3.66 (d, J=13.2 Hz, H_{2b}), 3.98 (d, J=4.1 Hz, H_1), 4.45 (d, J=5.9 Hz, H_7), 4.73 (d, J=5.9 Hz, H_8); MS *m/z* 284 (M^+). Found: C, 63.25; H, 8.62%. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51%.

Oxidation of ***11***: A mixture of **11** (12.0 g, 43.8 mmol), Na_2HPO_4 (103 g, 723 mmol), Na_2H_2edta (5 g), and CH_2Cl_2 (150 ml) was stirred at 0 °C and to this was added a CH_2Cl_2 solution of trifluoroperacetic acid (1.86 mol dm^{-3}, 118 ml, 219 mmol). After stirring for 12 h at 25 °C, the usual workup afforded a yellow residue. ^1H NMR analysis of this residue indicated that (1*R**,6*S**,7*S**,8*S**)-7,8-isopropylidenedioxy-1-phenyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**14a**) and (1*S**,6*R**,7*S**,8*S**)-7,8-isopropylidenedioxy-6-phenyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**14b**) were in 88:12 ratio. Purification of the residue on a silica-gel column using a 1:1 ether–petroleum ether mixture afforded **14a** (10.6 g, 84%) and **14b** (1.2 g, 9%). Total yield was 93% (11.8 g). **14a**: Mp 156—158 °C (chloroform–hexane); R_f=0.27 (1:1 ether–petroleum ether); IR 1735 cm^{-1} (C=O); ^1H NMR (C_6D_6) δ 1.13 and 1.30 (s, isopropylidene CH_3), 2.45 (m, H_5), 3.75 (d, J=13.5 Hz, H_{2a}), 4.01 (d, J=13.5 Hz, H_{2b}), 4.13 (m, H_6), 4.61 (d, J=6.0 Hz, H_7), 4.95 (d, J=6.0 Hz, H_8), 7.0—7.5 (m, C_6H_5); MS *m/z* 290 (M^+). Found: C, 66.09; H, 6.22%. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25%. **14b**: Mp 153—154 °C (chloroform–hexane); R_f=0.19 (1:1 ether–petroleum ether); IR 1733 cm^{-1} (C=O); ^1H NMR (C_6D_6) δ 0.99 and 1.10 (s, isopropylidene CH_3), 2.62 (d, J=15.5 Hz, H_{5a}), 3.15 (d, J=15.5 Hz, H_{5b}), 3.44 (dd, J=4.1, 13.5 Hz, H_{2a}), 3.69 (d, J=13.5 Hz, H_{2b}), 4.11 (d, J=4.1 Hz, H_1), 4.79 (d, J=5.8 Hz, H_7), 4.85 (d, J=5.8 Hz, H_8), 7.0—7.5 (m, C_6H_5); MS *m/z* 290 (M^+). Found: C, 65.54; H, 6.10%. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25%.

Baeyer-Villiger Oxidation of γ-Substituted Ketones. A. Results in Table 2: General. Unless otherwise stated, the Baeyer-Villiger oxidation was performed as follows. A mixture of a ketonic substrate (1 equiv), Na_2HPO_4 (9 equiv), and CH_2Cl_2 (3 ml/1 equiv of ketone) was cooled in an ice bath and stirred magnetically. To this was added dropwise a 1.0 mol dm^{-3} CH_2Cl_2 solution of trifluoroperacetic acid (3 equiv). The resulting mixture was stirred for 12 h at 25 °C and diluted with CH_2Cl_2 (5—10 ml/1 equiv of ketone). To this was added $Na_2S_2O_3 \cdot 5H_2O$ (0.8—1.6 g/1 equiv of ketone) at 0 °C and the mixture was stirred for 3 h at 25 °C. The insoluble material was removed by filtration and the filtrate was evaporated to give a crude product. The corresponding lactonic products were obtained as a mixture of two regioisomers. The isomeric ratio was determined by ^1H NMR and listed in Table 2. The regioisomers were separated by the silica-gel column chromatography and HPLC progress. The progress of elution of column chromatography was monitored by analytical TLC and fractions containing the desired product were combined and evaporated. Samples for elemental analysis were obtained by recrystallizations of the chromatographed products.

Typical Procedure. Oxidation of ***15***: Trifluoroperacetic acid in CH_2Cl_2 solution (1.0 mol dm^{-3}, 2.8 ml, 2.8 mmol) was added to a stirred, ice-cooled mixture of Na_2HPO_4 (1.20 g, 8.42 mmol) and **15** (320 mg, 0.936 mmol) in CH_2Cl_2 (2.8 ml). The mixture was stirred for 12 h at 25 °C and diluted with CH_2Cl_2 (10 ml). To this was added $Na_2S_2O_3 \cdot 5H_2O$ (1.5 g) at 0 °C and the resulting mixture was stirred for 3 h at 25 °C. The insoluble material was removed by filtration and the filtrate was evaporated. The residue (343 mg, 100%) consisted of (1*S**,6*S**,7*S**,8*S**)-1-*t*-butyldimethylsiloxymethyl-7,8-isopropylidenedioxy-3,9-dioxabicyclo[4.2.1]-nonan-4-one (**23a**) and (1*S**,6*S**,7*S**,8*S**)-6-*t*-butyldimethylsiloxymethyl-7,8-isopropylidenedioxy-3,9-dioxabicyclo[4.2.1]-nonan-4-one (**23b**) (55:45 ratio as determined by ^1H NMR analysis). Silica-gel column chromatography (1:1 ether–hexane) gave samples of **23a** and **23b**. **23a**: Mp 75—76 °C (ether–hexane); R_f=0.50 (3:1 ether–petroleum ether); IR 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.08 (s, *t*-$C_4H_9(C\underline{H}_3)_2Si$), 0.91 (s, *t*-$C_4\underline{H}_9(CH_3)_2Si$), 1.32 and 1.49 (s, isopropylidene CH_3), 2.99 (m, H_5), 3.61 (d, J=10.5 Hz, $\underline{H}_aH_bCOSi$), 3.95 (d, J=10.5 Hz, $H_a\underline{H}_bCOSi$), 4.30 (d, J=13.2 Hz, H_{2a}), 4.31 (t-like, J=3.8 Hz, H_6), 4.58 (d, J=13.2 Hz, H_{2b}), 4.68 (d, J=6.0 Hz, H_7), 4.86 (d, J=6.0 Hz, H_8). Found: *m/z* 343.1601. Calcd for $C_{16}H_{27}O_6Si$: ($M-CH_3$), 343.1575. **23b**: Mp 64—65 °C (ether–hexane); R_f=0.38 (3:1 ether–petroleum ether); IR 1738 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.09 (s, *t*-$C_4H_9(C\underline{H}_3)_2Si$), 0.92 (s, *t*-$C_4\underline{H}_9(CH_3)_2Si$), 1.32 and 1.49 (s, isopropylidene CH_3), 2.92 (d, J=16.0 Hz, H_{5a}), 3.23 (d, J=16.0 Hz, H_{5b}), 3.65 (d, J=10.5 Hz, $\underline{H}_aH_bCOSi$), 3.90 (d, J=10.5 Hz, $H_a\underline{H}_bCOSi$), 4.29—4.53 (m, H_1 and H_2), 4.60 (d, J=5.9 Hz, H_7), 5.00 (d, J=5.9 Hz, H_8). Found: *m/z* 343.1573. Calcd for $C_{16}H_{27}O_6Si$: ($M-CH_3$), 343.1575.

Oxidation of ***16***: Oxidation of **16** under the standard conditions afforded (1*R**,6*S**,7*S**,8*S**)-1-benzyloxymethyl-7,8-isopropylidenedioxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**24a**) and (1*S**,6*S**,7*S**,8*S**)-6-benzyloxymethyl-7,8-isopropylidenedioxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**24b**). **24a**: Mp 107—108 °C (ether–hexane); R_f=0.39 (3:1 ether–petroleum ether); IR 1736 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.33 and 1.48 (s, isopropylidene CH_3), 3.00 (m, H_5), 3.57 (d, J=10.0 Hz, $\underline{H}_aH_bCOCH_2C_6H_5$), 3.80 (d, J=10.0 Hz, $H_a\underline{H}_bCOCH_2C_6H_5$), 4.34 (m, H_6), 4.44 (d-like, J=3.2 Hz, H_2), 4.62 (d-like, J=2.0 Hz, $C\underline{H}_2C_6H_5$), 4.68 (d, J=6.0 Hz, H_7), 4.90 (d, J=6.0 Hz, H_8), 7.34 (s, C_6H_5). Found: C, 64.74; H, 6.69%. Calcd for $C_{18}H_{22}O_6$: C, 64.65; H, 6.63%. **24b**: Colorless oil; R_f=0.29 (3:1 ether–petroleum ether); IR 1736 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.36 and 1.52 (s, isopropylidene CH_3), 3.07 (d, J=16.0 Hz, H_{5a}), 3.25 (d, J=16.0 Hz, H_{5b}), 3.62 (d, J=10.0 Hz, $\underline{H}_aH_bCOCH_2C_6H_5$), 3.76 (d, J=10.0 Hz, $H_a\underline{H}_bCOCH_2C_6H_5$), 4.19—4.57 (m, H_1 and H_2), 4.59 (d, J=12.0 Hz, $H_a\underline{H}_bCC_6H_5$), 4.68 (d, J=6.0 Hz, H_7), 4.77 (d, J=12.0 Hz, $H_a\underline{H}_bCC_6H_5$), 5.05 (d, J=6.0 Hz, H_8), 7.39 (s, C_6H_5). Found: *m/z* 334.1415. Calcd for $C_{18}H_{22}O_6$: M, 334.1415.

Oxidation of ***17***: Oxidation of **17** afforded (1*R**,6*S**,7*S**,8*S**)-1-acetoxymethyl-7,8-isopropylidenedioxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**25a**) and (1*S**,6*S**,7*S**,8*S**)-6-acetoxymethyl-7,8-isopropylidenedioxy-3,9-dioxabicyclo[4.2.1]-

nonan-4-one (**25b**). **25a**: Mp 131—132 °C (ether–hexane); R_f=0.18 (3:1 ether–petroleum ether); IR 1739 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.33 and 1.50 (s, isopropylidene CH_3), 2.12 (s, CH_3CO), 3.02 (m, H_5), 4.10—4.50 (m, H_6, H_2, and CH_2OC=O), 4.72 (d, J=5.8 Hz, H_7), 4.91 (d, J=5.8 Hz, H_8); (C_6D_6) δ 1.00 and 1.32 (s, isopropylidene CH_3), 1.59 (s, CH_3CO), 2.32 (m, H_5), 3.71 (d, J=13.5 Hz, H_{2a}), 2.91 (d, J=13.5 Hz, H_{2b}), 3.97 (m, H_6), 4.14 (d, J=11.8 Hz, $\underline{H}_aH_bCOC$=O), 4.36 (d, J=11.8 Hz, $H_a\underline{H}_bCOC$=O), 4.43 (d, J=6.0 Hz, H_7), 4.61 (d, J=6.0 Hz, H_8). Found: C, 54.46; H, 6.32%. Calcd for $C_{13}H_{18}O_7$: C, 54.54; H, 6.34%. **25b**: Mp 151—153 °C (ether–hexane); R_f=0.16 (3:1 ether–petroleum ether); IR 1738 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.32 and 1.49 (s, isopropylidene CH_3), 2.11 (s, CH_3CO), 3.03 (s, H_5), 4.09—4.57 (m, H_1, H_2, and CH_2OC=O), 4.65 (d, J=5.7 Hz, H_7), 5.01 (d, J=5.7 Hz, H_8); (C_6D_6) δ 1.01 and 1.33 (s, isopropylidene CH_3), 1.63 (s, CH_3CO), 2.51 (d, J=13.8 Hz, H_{5a}), 2.91 (d, J=13.8 Hz, H_{5b}), 3.34 (dd, J=4.0, 13.8 Hz, H_{2a}), 3.60 (d, J=13.8 Hz, H_{2b}), 3.95 (d, J=4.0 Hz, H_1), 4.22 (d, J=11.5 Hz, $\underline{H}_aH_bCOC$=O), 4.40 (d, J=11.5 Hz, $H_a\underline{H}_bCOC$=O), 4.50 (d, J=5.8 Hz, H_7), 4.64 (d, J=5.8 Hz, H_8). Found: C, 54.57; H, 6.43%. Calcd for $C_{13}H_{18}O_7$: C, 54.54; H, 6.34%.

Oxidation of ***18***: Oxidation of **18** gave (1*S**,6*S**,7*S**,8*S**)-7,8-isopropylidenedioxy-1-pivaloyloxymethyl-3,9-dioxabicyclo-[4.2.1]nonan-4-one (**26a**) and (1*S**,6*S**,7*S**,8*S**)-7,8-isopropylidenedioxy-6-pivaloyloxymethyl-3,9-dioxabicyclo-[4.2.1]nonan-4-one (**26b**). **26a**: Mp 113—114 °C (ether–hexane); R_f=0.41 (3:1 ether–petroleum ether); IR 1732 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.20 (s, t-C_4H_9), 1.30 and 1.45 (s, isopropylidene CH_3), 2.98 (d-like, J=4.0 Hz, H_5), 4.00—4.51 (m, H_2, H_6, and CH_2OC=O), 4.70 (d, J=6.0 Hz, H_7), 4.90 (d, J=6.0 Hz, H_8); (C_6D_6) δ 0.98 and 1.30 (s, isopropylidene CH_3), 1.09 (s, t-C_4H_9), 2.29 (m, H_5), 3.76 (d, J=14.0 Hz, H_{2a}), 3.92 (m, H_6), 3.94 (d, J=14.0 Hz, H_{2b}), 4.14 (d, J=11.9 Hz, $\underline{H}_aH_bCOC$=O), 4.38 (d, J=11.9 Hz, $H_a\underline{H}_bCOC$=O), 4.43 (d, J=6.0 Hz, H_7), 4.58 (d, J=6.0 Hz, H_8). Found: C, 58.30; H, 7.34%. Calcd for $C_{16}H_{24}O_7$: C, 58.52; H, 7.37%. **26b**: Mp 121—122 °C (ether–hexane); R_f=0.32 (3:1 ether–petroleum ether); IR 1732 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.22 (s, t-C_4H_9), 1.30 and 1.48 (s, isopropylidene CH_3), 3.00 (s, H_5), 4.04—4.50 (m, H_1, H_2, and CH_2OC=O), 4.63 (d, J=5.5 Hz, H_7), 5.00 (d, J=5.5 Hz, H_8); (C_6D_6) δ 1.00 and 1.31 (s, isopropylidene CH_3), 1.14 (s, t-C_4H_9), 2.56 (d, J=15.7 Hz, H_{5a}), 2.92 (d, J=15.7 Hz, H_{5b}), 3.34 (dd, J=4.0, 13.5 Hz, H_{2a}), 3.58 (d, J=13.5 Hz, H_{2b}), 3.94 (d, J=4.0 Hz, H_1), 4.24 (d, J=11.5 Hz, $\underline{H}_aH_bCOC$=O), 4.40 (d, J=11.5 Hz, $H_a\underline{H}_bCOC$=O), 4.48 (d, J=6.0 Hz, H_7), 4.64 (d, J=6.0 Hz, H_8). Found: C, 58.68; H, 7.52%. Calcd for $C_{16}H_{24}O_7$: C, 58.52; H, 7.37%.

Oxidation of ***19***: The reaction of **19** afforded (1*S**,6*S**,7*S**,8*S**)-1-benzoyloxymethyl-7,8-isopropylidenedioxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**27a**) and (1*S**,6*S**,7*S**,8*S**)-6-benzoyloxymethyl-7,8-isopropylidenedioxy-3,9-dioxabicyclo-[4.2.1]nonan-4-one (**27b**). **27a**: Mp 171—173 °C (chloroform–hexane); R_f=0.34 (3:1 ether–petroleum ether); IR 1728 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.34 and 1.50 (s, isopropylidene CH_3), 3.03 (m, H_5), 4.30—4.60 (m, H_2, H_6, and CH_2OC=O), 4.71 (d, J=5.9 Hz, H_7), 4.99 (d, J=5.9 Hz, H_8), 7.48—8.03 (m, C_6H_5); (C_6D_6) δ 0.99 and 1.31 (s, isopropylidene CH_3), 2.30 (m, H_5), 3.78 (d, J=13.5 Hz, H_{2a}), 3.92 (m, H_6), 3.99 (d, J=13.5 Hz, H_{2b}), 4.37 (d, J=6.0 Hz, $\underline{H}_aH_bCOC$=O), 4.50 (d, J=6.0 Hz, H_7 and $H_a\underline{H}_bCOC$=O), 4.65 (d, J=6.0 Hz, H_8), 7.16 and 8.08 (m, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 24.70, 26.07, 42.37, 64.35, 73.46, 78.60, 82.23, 84.52, 85.88, 113.16, 128.55, 129.76, 133.32, 165.79, 171.80. Found: C, 62.30; H, 5.79%. Calcd for $C_{18}H_{20}O_7$: C, 62.06; H, 5.79%. **27b**: Mp 162—163 °C (chloroform–hexane); R_f=0.27 (3:1 ether–hexane); IR 1727 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.34 and 1.52 (s, isopropylidene CH_3), 3.14 (s, H_5), 4.18—4.69 (m, H_1, H_2, and CH_2OC=O), 4.73 (d, J=6.0 Hz, H_7), 5.06 (d, J=6.0 Hz, H_8), 7.50 and 8.08 (m, C_6H_5); (C_6D_6) δ 0.94 and 1.27 (s, isopropylidene CH_3), 2.54 (d, J=15.6 Hz, H_{5a}), 2.95 (d, J=15.6 Hz, H_{5b}), 3.28 (dd, J=4.0, 14.0 Hz, H_{2a}), 3.54 (d, J=14.0 Hz, H_{2b}), 4.92 (d, J=4.0 Hz, H_1), 4.27—4.74 (m, H_7, H_8, and CH_2OC=O), 7.09 and 8.09 (m, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 24.55, 25.98, 55.23, 65.98, 71.24, 82.27, 82.88, 83.93, 113.32, 128.52, 129.77, 133.27, 165.89, 171.39. Found: C, 61.84; H, 5.76%. Calcd for $C_{18}H_{20}O_7$: C, 62.06; H, 5.79%.

Oxidation of ***20***: The reaction of **20** produced (1*S**,6*S**,7*S**,8*S**)-7,8-isopropylidenedioxy-1-trifluoroacetoxymethyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**28a**) and (1*S**,6*S**,7*S**,8*S**)-7,8-isopropylidenedioxy-6-trifluoroacetoxymethyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**28b**). **28a**: Mp 139—141 °C (ether–hexane); R_f=0.41 (3:1 ether–petroleum ether); IR 1781 and 1737 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.31 and 1.48 (s, isopropylidene CH_3), 3.00 (d-like, J=3.7 Hz, H_5), 4.37 (s, CH_2OC=O), 4.37 (m, H_6), 4.40 (d, J=12.0 Hz, H_{2a}), 4.63 (d, J=12.0 Hz, H_{2b}), 4.71 (d, J=5.9 Hz, H_7), 4.92 (d, J=5.9 Hz, H_8); (C_6D_6) δ 0.96 and 1.28 (s, isopropylidene CH_3), 2.24 (m, H_5), 3.64 (s, H_2), 3.89 (m, H_6), 4.09 (d, J=12.0 Hz, $\underline{H}_aH_bCOC$=O), 4.24 (d, J=12.0 Hz, $H_a\underline{H}_bCOC$=O), 4.33 (d, J=6.0 Hz, H_7), 4.48 (d, J=6.0 Hz, H_8). Found: C, 45.70; H, 4.30%. Calcd for $C_{13}H_{15}O_7F_3$: C, 45.89; H, 4.44%. **28b**: Mp 130—132 °C (ether–hexane); R_f=0.34 (3:1 ether–petroleum ether); IR 1781 and 1738 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.32 and 1.50 (s, isopropylidene CH_3), 3.06 (s, H_5), 4.18—4.58 (m, H_1, H_2, and CH_2OC=O), 4.68 (d, J=5.3 Hz, H_7), 5.04 (d, J=5.3 Hz, H_8); (C_6D_6) δ 0.92 and 1.26 (s, isopropylidene CH_3), 2.41 (d, J=15.1 Hz, H_{5a}), 2.64 (d, J=15.1 Hz, H_{5b}), 3.20 (dd, J=4.0, 13.0 Hz, H_{2a}), 3.42 (d, J=13.0 Hz, H_{2b}), 3.82 (d, J=4.0 Hz, H_1), 4.07 (d, J=11.8 Hz, $\underline{H}_aH_bCOC$=O), 4.27 (d, J=11.8 Hz, $H_a\underline{H}_bCOC$=O), 4.31 (d, J=5.9 Hz, H_7), 4.51 (d, J=5.9 Hz, H_8). Found: C, 46.01; H, 4.30%. Calcd for $C_{13}H_{15}O_7F_3$: C, 45.89; H, 4.44%.

Oxidation of ***21***: Oxidation of **21** afforded (1*S**,6*S**,7*S**,8*S**)-7,8-isopropylidenedioxy-1-mesyloxymethyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**29a**) and (1*S**,6*S**,7*S**,8*S**)-7,8-isopropylidenedioxy-6-mesyloxymethyl-3,9-dioxabicyclo-[4.2.1]nonan-4-one (**29b**). **29a**: Mp 134—135 °C (chloroform–hexane); R_f=0.39 (2:1 ethyl acetate–hexane); IR 1738 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.30 and 1.49 (s, isopropylidene CH_3), 2.92—3.18 (m, H_5), 3.06 (s, CH_3SO_2), 4.18—4.53 (m, H_2, H_6, and CH_2OSO_2), 4.70 (d, J=5.9 Hz, H_7), 4.90 (d, J=5.9 Hz, H_8); (C_6D_6) δ 0.90 and 1.24 (s, isopropylidene CH_3), 2.18 (s, CH_3SO_2), 2.12—2.28 (m, H_5), 3.61 (d, J=13.8 Hz, H_{2a}), 3.74 (m, H_6), 4.78 (d, J=13.8 Hz, H_{2b}), 4.11 (s, CH_2OSO_2), 4.31 (d, J=5.9 Hz, H_7), 4.39 (d, J=5.9 Hz, H_8). Found: C, 44.61; H, 5.56; S, 10.21%. Calcd for $C_{12}H_{18}O_8S$: C, 44.72; H, 5.63; S, 9.95%. **29b**: Mp 137—138 °C (chloroform–hexane); R_f=0.33 (2:1 ethyl acetate–hexane); IR 1739 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.31 and 1.50 (s, isopropylidene CH_3), 3.07 (s, CH_3SO_2 and H_5), 4.20—4.53 (m, H_1, H_2, and CH_2OSO_2), 4.65 (d, J=6.0 Hz, H_7), 5.01 (d, J=6.0 Hz, H_8); (C_6D_6) δ 0.90 and 1.25 (s, isopropylidene CH_3), 2.21 (s, CH_3SO_2), 2.42 (d, J=16.0 Hz, H_{5a}), 2.85 (d, J=16.0 Hz, H_{5b}), 3.20 (dd, J=4.0, 13.1 Hz, H_{2a}), 3.44 (d, J=13.1 Hz, H_{2b}), 3.84 (d, J=4.0 Hz, H_1), 4.02 (d, J=11.0 Hz, $\underline{H}_aH_bCOSO_2$), 4.20

(d, J=11.0 Hz, $H_aH_bCOSO_2$), 4.28 (d, J=6.0 Hz, H_7), 4.51 (d, J=6.0 Hz, H_8). Found: C, 44.35; H, 5.52%; S, 10.11%. Calcd for $C_{12}H_{18}O_8S$: C, 44.72; H, 5.63; S, 9.95%.

Oxidation of ***22***: Oxidation of **22** produced (1*S**,6*S**,7*S**,8*S**)-7,8-isopropylidenedioxy-1-trifluoromesyloxymethyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**30a**) and (1*S**,6*S**,7*S**,8*S**)-7,8-isopropylidenedioxy-6-trifluoromesyloxymethyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**30b**). **30a**: colorless oil; R_f=0.32 (3:1 ether–hexane); IR 1740 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.29 and 1.48 (s, isopropylidene CH_3), 3.01 (d-like, J=3.5 Hz, H_5), 4.38 (s, H_2), 4.53 (d, J=10.3 Hz, $H_aH_bCOSO_2$), 4.70 (d, J=10.3 Hz, $H_aH_bCOSO_2$), 4.71 (d, J=5.6 Hz, H_7), 4.91 (d, J=5.6 Hz, H_8); (C_6D_6) δ 0.87 and 1.20 (s, isopropylidene CH_3), 2.04 (dd, J=3.0, 16.1 Hz, H_{5a}), 2.21 (dd, J=5.9, 16.1 Hz, H_{5b}), 3.51 (s, H_2), 4.79 (dd, J=3.0, 5.9 Hz, H_6), 4.04—4.44 (m, H_7, H_8, and CH_2OSO_2). Found: m/z 376.0436. Calcd for $C_{12}H_{15}O_8SF_3$: M, 376.0440. **30b**: Mp 80—83 °C (ether–hexane); R_f=0.27 (3:1 ether–hexane); IR 1740 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.30 and 1.48 (s, isopropylidene CH_3), 2.99 (d, J=16.0 Hz, H_{5a}), 3.17 (d, J=16.0 Hz, H_{5b}), 4.33—4.62 (m, H_1, H_2, and CH_2OSO_2), 4.67 (d, J=5.8 Hz, H_7), 5.03 (d, J=5.8 Hz, H_8); (C_6D_6) δ 0.93 and 1.23 (s, isopropylidene CH_3), 2.42 (d, J=16.0 Hz, H_{5a}), 2.67 (d, J=16.0 Hz, H_{5b}), 3.28 (dd, J=3.7, 13.9 Hz, H_{2a}), 3.49 (d, J=13.9 Hz, H_{2b}), 3.87 (d, J=3.7 Hz, H_1), 4.28 (d, J=5.8 Hz, H_7), 4.42 (s, CH_2OSO_2), 4.53 (d, J=5.8 Hz, H_8). Found: m/z 376.0423. Calcd for $C_{12}H_{15}O_3SF_3$: M, 376.0440.

Oxidation of ***37***: Oxidation of **37** gave (1*R**,6*R**,8*S**)-8-benzoyloxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**42a**) and (1*R**,6*R**,7*S**)-7-benzoyloxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**42b**). **42a**: Mp 137—138 °C (chloroform–hexane); R_f=0.34 (3:1 ether–benzene); V_R=6.4 ml (9:1 ether–petroleum ether); IR 1738 and 1719 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.44 (t-like, J=5.8 Hz, H_7), 2.91 (dd, J=4.6, 16.0 Hz, H_{5a}), 3.13 (dd, J=2.7, 16.0 Hz, H_{5b}), 4.28—4.62 (m, H_1 and H_2), 4.69 (m, H_6), 5.73 (dd, J=5.0, 5.5 Hz, H_8), 7.51 and 8.04 (m, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 37.54, 45.19, 71.57, 72.77, 75.87, 82.47, 128.35, 129.56, 133.20, 166.29, 172.48. Found: C, 64.41; H, 5.40%. Calcd for $C_{14}H_{15}O_5$: C, 64.11; H, 5.38%. **42b**: Mp 128—130 °C (chloroform–hexane); R_f=0.29 (3:1 ether–benzene); V_R=7.8 ml (9:1 ether–petroleum ether); IR 1735 and 1719 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.32 (ddd, J=3.1, 8.5, 14.0 Hz, H_{8a}), 2.78 (ddd, J=1.2, 7.3, 14.0 Hz, H_{8b}), 2.95 (dd, J=2.2, 15.9 Hz, H_{5a}), 3.21 (dd, J=5.0, 15.9 Hz, H_{5b}), 4.12 (dd, J=4.0, 15.9 Hz, H_{2a}), 4.44 (m, H_6), 4.47 (d, J=15.9 Hz, H_{2b}), 4.76 (m, H_1), 5.38 (dd, J=3.1, 7.3 Hz, H_7), 7.47 and 8.02 (m, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 33.68, 43.06, 73.05, 77.85, 78.12, 78.27, 128.50, 129.74, 133.35, 166.25, 172.15. Found: C, 64.01; H, 5.40%. Calcd for $C_{14}H_{14}O_5$: C, 64.11; H, 5.38%.

Oxidation of ***34***: Oxidation of **34** led to (1*R**,6*R**,8*S**)-8-*t*-butyldimethylsiloxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**39a**) and (1*R**,6*R**,7*S**)-7-*t*-butyldimethylsiloxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**39b**). **39a**: Mp 70—72 °C (ether–hexane); R_f=0.18 (1:1 ether–hexane); V_R=20.0 ml (5:1 hexane–ethyl acetate); IR 1738 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 0.03 (s, *t*-$C_4H_9(C\underline{H}_3)_2Si$), 0.90 (s, *t*-$C_4\underline{H}_9(CH_3)_2Si$), 1.4—2.5 (m, H_7), 2.81 (dd, J=5.0, 16.0 Hz, H_{5a}), 3.06 (dd, J=2.3, 16.0 Hz, H_{5b}), 4.18—4.43 (m, H_1 and H_2), 4.63 (m, H_6), 4.75 (dd, J=3.4, 6.9 Hz, H_8). **39b**: Mp 48—51 °C (ether–hexane); R_f=0.18 (1:1 ether–hexane); V_R=23.6 ml (5:1 hexane–ethyl acetate); IR 1735 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 0.02 (s, *t*-$C_4H_9(C\underline{H}_3)_2Si$), 0.87 (s, *t*-$C_4\underline{H}_9(CH_3)_2Si$), 2.30—2.69 (m, H_8), 2.92 (m, H_5), 4.06 (dd, J=4.1, 13.8 Hz, H_{2a}), 4.12 (m, H_6), 4.40 (dd, J=3.0, 7.0 Hz, H_7), 4.42 (d, J=13.8 Hz, H_{2b}), 4.68 (m, H_1).

Regioisomeric ratio of **39a** and **39b** was determined as follows. To a solution of the lactones (53 mg, 0.195 mmol) in THF (1.0 ml) was added $(n\text{-}C_4H_9)_4NF$ in THF (0.822 mol dm^{-3} solution, 0.356 ml, 0.293 mmol) at 15 °C under argon. After stirring for 20 min, the reaction mixture was worked up to give a yellow oil. To this oil dissolved in pyridine (1 ml) was added benzoyl chloride (0.048 ml, 0.39 mmol) at 0 °C under argon. After stirring for 12 h at 15 °C, the reaction mixture was worked up to give a mixture of **42a** and **42b** (50 mg) as an oil. This oil was analyzed by HPLC.

Oxidation of ***33***: Oxidation of **33** afforded (1*R**,6*R**,8*S**)-8-benzyloxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**38a**) and (1*R**,6*R**,7*S**)-7-benzyloxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**38b**). This mixture was subjected to elemental analysis. Found: C, 67.38; H, 6.51%. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50%. **38a**: colorless oil; R_f=0.19 (6:1 ether–hexane); V_R=19.0 ml (2:1 hexane–ethyl acetate); IR 1738 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.75 (t-like, J=5.0 Hz, H_7), 2.94 (m, H_5), 4.1—4.7 (m, H_1, H_2, H_6, and H_8), 7.29 (s, C_6H_5). **38b**: Mp 103—104 °C (ether–hexane); R_f=0.19 (6:1 ether–hexane); V_R=20.4 ml (2:1 hexane–ethyl acetate); IR 1739 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.0—2.7 (m, H_8), 2.88 (d-like, J=3.5 Hz, H_5), 4.02 (dd, J=4.0, 13.9 Hz, H_{2a}), 4.19 (dd, J=4.1, 7.8 Hz, H_7), 4.30 (m, H_6), 4.40 (d, J=13.9 Hz, H_{2b}), 4.48 (s, $C\underline{H}_2C_6H_5$), 4.64 (m, H_1), 7.32 (s, C_6H_5).

Ratio of **38a** and **38b** was determined as follows. The mixture of lactones (20 mg, 0.0862 mmol), 10% Pd/C (2 mg), and ethyl acetate (1 ml) was stirred for 12 h at 15 °C under atmospheric pressure of hydrogen. The insoluble material was removed by filtration and the filtrate was evaporated to give a colorless oil. To this oil dissolved in pyridine (0.44 ml) was added benzoyl chloride (0.021 ml, 0.172 mmol) at 0 °C under argon. After stirring for 10 h at 15 °C, the reaction mixture was worked up to give a mixture of **42a** and **42b** (22 mg) as a yellow oil, which was analyzed by HPLC.

Oxidation of ***35***: The reaction of **35** led to (1*R**,6*R**,8*S**)-8-acetoxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**40a**) and (1*R**,6*R**,7*S**)-7-acetoxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**40b**). This mixture was subjected to elemental analysis. Found: C, 54.01; H, 6.20%. Calcd for $C_9H_{12}O_5$: C, 53.99; H, 6.04%. **40a**: colorless oil; R_f=0.19 (7:1 ether–hexane); V_R=12.5 ml (1:1 hexane–ethyl acetate); IR 1735 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.08 (s, CH_3CO), 2.22—2.38 (m, H_7), 2.88 (dd, J=4.5, 15.1 Hz, H_{5a}), 3.12 (dd, J=2.7, 15.1 Hz, H_{5b}), 4.40 (s, H_2), 4.42 (m, H_1), 4.62 (m, H_6), 5.47 (dd, J=4.0, 6.5 Hz, H_8). **40b**: Mp 80—82 °C (ether–hexane); R_f=0.14 (7:1 ether–hexane); V_R=14.0 ml (1:1 hexane–ethyl acetate); IR 1738 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.07 (s, CH_3CO), 2.10—2.34 (m, H_{8a}), 2.64 (dd, J=7.9, 14.2 Hz, H_{8b}), 2.89 (dd, J=2.9, 15.1 Hz, H_{5a}), 3.14 (dd, J=4.5, 15.1 Hz, H_{5b}), 4.10 (dd, J=4.1, 13.6 Hz, H_{2a}), 4.31 (m, H_6), 4.44 (d, J=13.6 Hz, H_{2b}), 4.70 (m, H_1), 5.13 (dd, J=3.0, 7.9 Hz, H_7).

Oxidation of ***36***: Oxidation of **36** gave (1*R**,6*R**,8*S**)-8-pivaloyloxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**41a**) and (1*R**,6*R**,7*S**)-7-pivaloyloxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**41b**). Elemental analyses of this mixture were: Found: C, 59.54; H, 7.78%. Calcd for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49%. **41a**: Colorless oil; R_f=0.24 (3:1 ether–hexane); V_R=12.2 ml (2:1 hexane–ethyl acetate); IR 1732 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 1.18 (s, *t*-C_4H_9), 2.0—2.7 (m, H_7),

2.85 (dd, J=5.0, 16.5 Hz, H_{5a}), 3.06 (dd, J=2.0, 16.5 Hz, H_{5b}), 4.32 (m, H_1), 4.36 (s, H_2), 4.58 (m, H_6), 5.45 (dd, J=3.7, 6.8 Hz, H_8). **41b**: Mp 82—83 °C (ether–hexane); R_f=0.22 (3:1 ether–hexane); V_R=15.3 ml (2:1 hexane–ethyl acetate); IR 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.18 (s, t-C_4H_9), 2.08 (ddd, J=3.2, 8.0, 13.8 Hz, H_{8a}), 2.63 (dd, J=7.8, 13.8 Hz, H_{8b}), 2.87 (dd, J=3.0, 16.0 Hz, H_{5a}), 3.15 (dd, J=4.8, 16.0 Hz, H_{5b}), 4.08 (dd, J=4.0, 13.1 Hz, H_{2a}), 4.25 (m, H_6), 4.43 (d, J=13.1 Hz, H_{2b}), 4.67 (m, H_1), 5.10 (dd, J=3.2, 7.8 Hz, H_7).

B. Results of Table 3. General: The Baeyer-Villiger oxidation and workup were generally performed as follows. To a mixture of a ketone (1 equiv), Na_2HPO_4 (11.9—12.8 g/l equiv of ketone), and CH_2Cl_2 (2.0—2.5 ml/l equiv of ketone; for **43**, 60 mg/(1 equiv of the ketone) of Na_2H_2edta was used) was added 1.0 mol dm^{-3} CH_2Cl_2 solution of trifluoroperacetic acid (3 equiv) at 0 °C. After stirring for 36 h at 20 °C (at 25 °C for **43**), the mixture was diluted with CH_2Cl_2 (1.5—5.5 ml/l equiv of ketone). To this was added $Na_2S_2O_3\cdot5H_2O$ (0.66—1.6 g/l equiv of ketone) at 0 °C and the resulting mixture was stirred for 2 h at 20 °C (for 4 h at 25 °C for **43**). The insoluble material was removed by filtration and the filtrate was evaporated to give a solid. The residue was subjected to silica-gel column chromatography to afford the desired lactones and an unreached starting material. Elution course of the column chromatography was monitored by TLC. The lactone was obtained as a mixture of two regioisomers. The product ratio was determined by ^1H NMR (for **43**, **44**, and **46**) or HPLC (for **47**, **48**, **49**, and **50**) and given in Table 3. The isomers were separated by rechromatography on silica gel (except for **43**). Samples for elemental analysis were obtained by recrystallizations of chromatographed products.

Typical Procedure. Oxidation of 43: Trifluoroperacetic acid in CH_2Cl_2 (1.0 mol dm^{-3} solution, 141 ml, 141 mmol) was added dropwise to a stirred, ice-cooled mixture of Na_2HPO_4 (64.8 g, 569 mmol), Na_2H_2edta (3 g), **43** (10.0 g, 47.4 mmol), and CH_2Cl_2 (200 ml). The mixture was stirred for 36 h at 25 °C and diluted with CH_2Cl_2 (200 ml). To this was added $Na_2S_2O_3\cdot5H_2O$ (75 g) at 0 °C and the resulting mixture was stirred for 4 h at 25 °C. The insoluble material was removed by filtration and the filtrate was evaporated. Chromatography of the residue on a silica gel column using a 9:1 mixture of hexane and ethyl acetate to pure ethyl acetate afforded a 33:67 mixture (determined by ^1H NMR) of (1*R**,6*S**,7*R**,8*R**)-7,8-isopropylidenedioxy-8-methyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**51a**) and (1*S**,6*R**,7*R**,8*S**)-7,8-isopropylidenedioxy-7-methyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**51b**) (5.59 g, 52%, 84% based on consumed **43**). In addition, unreacted **43** was obtained (3.80 g). Compounds **51a** and **51b** were separated by fractional recrystallizations from hexane–chloroform. **51a**: Mp 129.5—130 °C; R_f=0.46 (1:1 hexane–ethyl acetate); IR 1736 cm^{-1} (C=O); ^1H NMR (C_6D_6) δ 1.32 (s, CH_3), 1.34 and 1.48 (s, isopropylidene CH_3), 2.24 (dd, J=3.0, 16.0 Hz, H_{5a}), 2.52 (dd, J=4.8, 16.0 Hz, H_{5b}), 3.38 (dd, J=3.2, 14.0 Hz, H_{2a}), 3.62 (d, J=14.0 Hz, H_{2b}), 3.78 (m, H_1 and H_6), 4.14 (s, H_7); ^{13}C NMR ($CDCl_3$) δ 20.24, 27.87, 29.07, 42.94, 70.51, 79.69, 85.62, 91.47, 113.19, 171.70. Found: C, 58.14; H, 7.22%. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07%. **51b**: Mp 132—133 °C; R_f=0.46 (1:1 hexane–ethyl acetate); IR 1731 cm^{-1} (C=O); ^1H NMR (C_6D_6) δ 1.28 (s, CH_3), 1.28 and 1.48 (s, isopropylidene CH_3), 2.26 (dd, J=3.2, 17.0 Hz, H_{5a}), 2.52 (dd, J=4.2, 17.0 Hz, H_{5b}), 3.38 (dd, J=3.3, 14.6 Hz, H_{2a}), 3.58 (d, J=14.6 Hz, H_{2b}), 3.82 (m, H_1 and H_6), 4.34 (s, H_8); ^{13}C NMR ($CDCl_3$) δ 19.62, 27.68, 28.68, 42.02, 71.88, 82.01, 84.44, 86.82, 92.19, 113.12, 172.83. Found: C, 57.93; H, 7.05%. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07%.

Oxidation of 44: The reaction of **44** formed (1*R**,6*S**,7*R**,8*R**)-7,8-isopropylidenedioxy-8-pentyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**52a**) and (1*S**,6*R**,7*R**,8*S**)-7,8-isopropylidenedioxy-7-pentyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**52b**). Elemental analysis was performed as a mixture of **52a** and **52b**. Found: C, 63.13; H, 8.56%. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51%. **52a**: R_f=0.56 (3:1 ether–petroleum ether); IR 1736 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.8—1.8 (m, n-C_5H_{11}), 1.36 and 1.50 (s, isopropylidene CH_3), 2.28 (dd, J=2.6, 16.2 Hz, H_{5a}), 2.52 (dd, J=5.0, 16.2 Hz, H_{5b}), 3.3—4.0 (m, H_1, H_2, and H_6), 4.20 (s, H_7). **52b**: R_f=0.50 (3:1 ether–petroleum ether); IR 1732 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.8—1.8 (m, n-C_5H_{11}), 1.30 and 1.49 (s, isopropylidene CH_3), 2.34 (dd, J=3.2, 16.8 Hz, H_{5a}), 2.62 (dd, J=4.0, 16.8 Hz, H_{5b}), 3.42 (dd, J=3.8, 13.6 Hz, H_{2a}), 3.64 (dd, J=1.2, 13.6 Hz, H_{2b}), 3.80 (d-like, J=3.2 Hz, H_6), 3.96 (t-like, J=3.2 Hz, H_1), 4.44 (s, H_8).

Oxidation of 45: To a mixture of **45** (252 mg, 0.992 mmol), Na_2HPO_4 (1.81 g, 12.7 mmol), and CH_2Cl_2 (2.0 ml) was added dropwise trifluoroperacetic acid in CH_2Cl_2 (1.0 mol dm^{-3} solution, 3.0 ml, 3.0 mmol) at 0 °C. After stirring for 36 h at 20 °C, the reaction mixture was worked up as usual to give 220 mg of a white solid. TLC and NMR analysis of this solid indicated complete recovery of the starting material.

Oxidation of 46: Oxidation of **46** afforded (1*R**,6*S**,7*R**,8*S**)-7,8-isopropylidenedioxy-8-phenyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**53a**) and (1*S**,6*R**,7*R**,8*S**)-7,8-isopropylidenedioxy-7-phenyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**53b**). **53a**: Mp 148—149 °C (chloroform–hexane); R_f=0.42 (3:1 ether–petroleum ether); IR 1738 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.02 and 1.50 (s, isopropylidene CH_3), 3.10 (m, H_5), 3.80 (dd, J=3.6, 13.8 Hz, H_{2a}), 4.28 (d, J=13.8 Hz, H_{2b}), 4.38 (m, H_6), 4.60 (d-like, J=3.2 Hz, H_1), 5.16 (s, H_7), 7.3—7.6 (m, C_6H_5). Found: C, 65.80; H, 6.31%. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25%. **53b**: Mp 142—143 °C (chloroform–hexane); R_f=0.28 (3:1 ether–petroleum ether); IR 1741 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.04 and 1.52 (s, isopropylidene CH_3), 2.44 (dd, J=4.2, 17.4 Hz, H_{5a}), 2.88 (dd, J=3.0, 17.4 Hz, H_{5b}), 4.4—4.6 (m, H_1, H_2, and H_6), 5.52 (s, H_8), 7.3—7.6 (m, C_6H_5). Found: C, 65.58; H, 6.29%. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25%.

Oxidation of 47: Oxidation of **47** gave (1*R**,6*S**,7*R**,8*S**)-8-t-butyldimethylsiloxymethyl-7,8-isopropylidenedioxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**54a**) and (1*S**,6*R**,7*R**,8*S**)-7-t-butyldimethylsiloxymethyl-7,8-isopropylidenedioxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**54b**). **54a**: Mp 99.0—100 °C (ether–hexane); R_f=0.48 (2:1 hexane–ethyl acetate); V_R=11.2 ml (4:1 hexane–ethyl acetate); IR 1732 cm^{-1} (C=O); ^1H NMR (C_6D_6) δ 0.08 (s, t-$C_4H_9(C\underline{H}_3)_2Si$), 0.96 (s, t-$C_4\underline{H}_9(CH_3)_2Si$), 1.38 and 1.54 (s, isopropylidene CH_3), 2.29 (dd, J=2.8, 16.2 Hz, H_{5a}), 2.54 (dd, J=5.0, 16.2 Hz, H_{5b}), 3.6—4.2 (m, H_1, H_2, and H_6), 4.00 (s, H_7), 4.20 (s, CH_2OSi); ^{13}C NMR ($CDCl_3$) δ 18.37, 25.93, 27.98, 28.92, 42.88, 65.83, 70.78, 79.98, 84.58, 85.85, 96.04, 113.96, 171.77. Found: C, 56.52; H, 8.30%. Calcd for $C_{17}H_{30}O_6Si$: C, 56.96; H, 8.44%. **54b**: Mp 79.0—80.0 °C (ether–hexane); R_f=0.40 (2:1 hexane–ethyl acetate); V_R=14.7 ml (4:1 hexane–ethyl acetate); IR 1735 cm^{-1} (C=O); ^1H NMR (C_6D_6) δ 0.08 (s, t-$C_4H_9(C\underline{H}_3)_2Si$), 0.95 (s, t-$C_4\underline{H}_9(CH_3)_2Si$), 1.39 and 1.56 (s, isopropylidene CH_3), 2.44 (dd, J=3.0, 16.8 Hz, H_{5a}), 3.02 (dd, J=4.2, 16.8 Hz, H_{5b}), 3.42 (dd, J=3.4, 13.6 Hz, H_{2a}), 3.62 (dd, J=1.0, 13.6 Hz, H_{2b}), 3.84 (d, J=3.0

Hz, CH_2OSi), 3.84 (m, H_6), 4.15 (m, H_1), 4.44 (s, H_8); ^{13}C NMR ($CDCl_3$) δ 18.40, 25.96, 27.90, 28.76, 41.53, 64.40, 71.70, 80.96, 83.48, 84.58, 96.54, 113.95, 172.93. Found: C, 56.88; H, 8.47%. Calcd for $C_{17}H_{30}O_6Si$: C, 56.96; H, 8.44%.

Oxidation of ***48***: Oxidation of **48** afforded (1*R**,6*S**,7*R**,8*S**)-8-benzyloxymethyl-7,8-isopropylidenedioxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**55a**) and (1*S**,6*R**,7*R**,8*S**)-7-benzyloxymethyl-7,8-isopropylidenedioxy-3,9-dioxabicyclo-[4.2.1]nonan-4-one (**55b**). **55a**: oil; R_f=0.50 (6:1 ether–petroleum ether); V_R=7.6 ml (3:2 petroleum ether–ethyl acetate); IR 1740 cm^{-1} (C=O); ^1H NMR (C_6D_6) δ 1.30 and 1.50 (s, isopropylidene CH_3), 2.24 (dd, J=2.5, 16.0 Hz, H_{5a}), 2.50 (dd, J=5.0, 16.0 Hz, H_{5b}), 3.52 (d, J=10.4 Hz, $\underline{H}_aH_bCOCH_2C_6H_5$), 3.84 (d, J=10.4 Hz, $H_a\underline{H}_bCOCH_2C_6H_5$), 3.6—4.2 (m, H_1, H_2, and H_6), 4.18 (s, H_7), 4.36 (s, $C\underline{H}_2C_6H_5$), 7.20 (s, C_6H_5). Found: *m/z* 334.1418. Calcd for $C_{18}H_{22}O_6$: M, 334.1416. **55b**: Mp 116—117 °C (chloroform–hexane); R_f=0.45 (6:1 ether–petroleum ether); V_R=8.67 ml (3:2 petroleum ether–ethyl acetate); IR 1740 cm^{-1} (C=O); ^1H NMR (C_6D_6) δ 1.29 and 1.50 (s, isopropylidene CH_3), 2.36 (dd, J=3.0, 16.6 Hz, H_{5a}), 2.98 (dd, J=4.2, 16.6 Hz, H_{5b}), 3.36 (dd, J=3.0, 14.0 Hz, H_{2a}), 3.56 (dd, J=1.4, 14.0 Hz, H_{2b}), 3.61 (s, $\underline{H}_2COCH_2C_6H_5$), 3.81 (d-like, J=3.0 Hz, H_6), 4.21 (m, H_1), 4.38 (s, H_8), 4.42 (s, $C\underline{H}_2C_6H_5$), 7.18 (s, C_6H_5). Found: C, 64.70; H, 6.68%. Calcd for $C_{18}H_{22}O_6$: C, 64.65; H, 6.63%.

Oxidation of ***49***: Oxidation of **49** led to (1*R**,6*S**,7*R**,8*S**)-7,8-isopropylidenedioxy-8-pivaloyloxymethyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (**56a**) and (1*S**,6*R**,7*R**,8*S**)-7,8-isopropylidenedioxy-7-pivaloyloxymethyl-3,9-dioxabicyclo-[4.2.1]nonan-4-one (**56b**). **56a**: Mp 137—138 °C (hexane–ethyl acetate); R_f=0.54 (6:1 ether–petroleum ether); V_R=12.2 ml (7:3 hexane–ethyl acetate); IR 1740 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.24 (t-C_4H_9), 1.44 and 1.50 (s, isopropylidene CH_3), 3.04 (d-like, J=3.5 Hz, H_5), 4.2—4.4 (m, H_1 and H_6), 4.32 (d, J=11.5 Hz, $\underline{H}_aH_bCOC$=O), 4.41 (s, H_2), 4.46 (s, H_7), 4.74 (d, J=11.5 Hz, $H_a\underline{H}_bCOC$=O). Found: C, 58.40; H, 7.44%. Calcd for $C_{16}H_{24}O_7$: C, 58.52; H, 7.37%. **56b**: Mp 131—132 °C (hexane–ethyl acetate); R_f=0.46 (6:1 ether–petroleum ether); V_R=15.0 ml (7:3 hexane–ethyl acetate); IR 1740 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.24 (s, t-C_4H_9), 1.44 and 1.50 (s, isopropylidene CH_3), 3.08 (d-like, J=3.6 Hz, H_5), 4.08 (d, J=12.5 Hz, $\underline{H}_aH_bCOC$=O), 4.2—4.5 (m, H_1 and H_6), 4.37 (s, H_2), 4.72 (d, J=12.5 Hz, $H_a\underline{H}_bCOC$=O), 4.80 (s, H_8). Found: C, 58.52; H, 7.30%. Calcd for $C_{16}H_{24}O_7$: C, 58.52; H, 7.37%.

Oxidation of ***50***: Oxidation of **50** afforded (1*R**,6*S**,7*R**,8*S**)-8-benzoyloxymethyl-7,8-isopropylidenedioxy-3,9-dioxabicyclo[4.2.1]nonan-4-one (**57a**) and (1*S**,6*R**,7*R**,8*S**)-7-benzoyloxymethyl-7,8-isopropylidenedioxy-3,9-dioxabicyclo-[4.2.1]nonan-4-one (**57b**). **57a**: Mp 196—197 °C (hexane–ethyl acetate); R_f=0.46 (6:1 ether–petroleum ether); V_R=9.54 ml (3:2 petroleum ether–ethyl acetate); IR 1730 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.42 and 1.50 (s, isopropylidene CH_3), 3.08 (d-like, J=4.0 Hz, H_5), 4.30 (t-like, J=3.6 Hz, H_6), 4.46 (s, H_2), 4.52 (m, H_1), 4.62 (s, H_7), 4.70 (d, J=12.6 Hz, $\underline{H}_aH_bCOC$=O), 4.86 (d, J=12.6 Hz, $H_a\underline{H}_bCOC$=O), 7.3—7.6 (m, C_6H_5). Found: *m/z*, 333.0923. Calcd for $C_{17}H_{17}O_7$: ($M-CH_3$), 333.0873. **57b**: Mp 189—190 °C (hexane–ethyl acetate); R_f=0.39 (6:1 ether–petroleum ether); V_R=11.2 ml (3:2 petroleum ether–ethyl acetate); IR 1734 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.42 and 1.50 (s, isopropylidene CH_3), 3.12 (d-like, J=4.0 Hz, H_5), 4.38 (s, H_2), 4.2—4.5 (m, H_1, H_6, and $\underline{H}_aH_bCOC$=O) 4.80 (d, J=12.8 Hz, $H_a\underline{H}_bCOC$=O), 4.94 (s, H_8), 7.3—7.6 (m, C_6H_5). Found: C, 60.68; H, 5.35%. Calcd for $C_{18}H_{20}O_7 \cdot 0.3H_2O$: C, 61.11; H, 5.86%.

Competitive reaction of ***43*** *and (1*R*,5S*,6S*,7R*)-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one.* To a mixture of (1*R**,5*S**,6*S**,7*R**)-6,7-isopropylidenedioxy-8-oxabicyclo[3.2.1]octan-3-one (1.07 g, 5 mmol),[21b] **43** (1.14 g, 5 mmol), Na_2HPO_4 (212 mg, 1.5 mmol), and CH_2Cl_2 (20 ml) was added CH_2Cl_2 solution of trifluoroperacetic acid (1.0 mol dm^{-3}, 1.0 ml, 1.0 mmol) at 0 °C. After stirring for 5 h at 20 °C, the mixture was diluted with CH_2Cl_2 (20 ml). To this was added $Na_2S_2O_3 \cdot 5H_2O$ (300 mg) at 0 °C and the mixture was stirred for 1 h at 20 °C. The reaction mixture was worked up in a usual way to give a white solid. HPLC analysis of the residue indicated that **51** (two regioisomers) and (1*R**,6*S**,7*S**,8*R**)-7,8-isopropylidenedioxy-3,9-dioxabicyclo[4.2.1]nonan-4-one were produced in 22:78 ratio. V_R (3:2 ethyl acetate–hexane): 9.3 ml (**51**), 10.7 ml (1*R**,6*S**,7*S**,8*R**)-7,8-isopropylidenedioxy-3,9-dioxabicyclo-[4.2.1]nonan-4-one.

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20) ^{13}C NMR shift of carbonyl carbon of the ketones is little affected by the nature of R. Typical substituents and the chemical shifts ($CDCl_3$, ppm downfield from $(CH_3)_4Si$ internal standard) follow: H, 204.32; *n*-C_5H_{11}, 205.07; C_6H_5, 204.54; $CH_2OSi(CH_3)_2$-*t*-C_4H_9, 204.60; $CH_2OCH_2C_6H_5$, 204.56; CH_2OCO-*t*-C_4H_9, 204.23; $CH_2OCOC_6H_5$, 204.20.

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