CH_2Cl_2. The organic layer was washed with a 5% HONa solution, dried, and evaporated. The diastereoisomeric excesses were determined on the crude product by NMR. Finally the product was purified by chromatography as in part A.

Desulfurization with Lithium/Ethylamine. General Procedure. β-Hydroxy sulfoxide (1 mmol) is dissolved in 10 mL of ethylamine under Argon and cooled at −78 °C. Then 30 mmol (0.21 g) of lithium were slowly added, and the reaction mixture was allowed to react till a persistant blue color was obtained. Ammonium chloride (0.8 g) was then added and the excess lithium was removed. After evaporation of the ethylamine, the residue was diluted with water and extracted with ether. After the usual workup, the product was purified by chromatography (eluent ether/hexane, 30/70).

Registry No. **1a**, 95482-76-1; **1b**, 95482-77-2; **1c**, 95482-78-3; **1d**, 95482-79-4; **2a**, 95482-80-7; **2b**, 95482-82-9; **2c**, 73773-39-4; **2d**, 95482-84-1; **3a**, 95482-81-8; **3b**, 95482-83-0; **3c**, 73766-48-0; **3d**, 95482-85-2; **4**, 1519-39-7; **5**, 4192-77-2; **6**, 95512-42-8; (*E*)-C_6H_5CH=CHCOCl, 17082-09-6; $(CH_3)_2C$=HCOCl, 3350-78-5; (*E*)-CH_3CH=$CHCO_2Et$, 623-70-1; (*E*)-$CH_3(CH_2)_6CH$=$CHCO_2Et$, 7367-88-6; (*S*)-(*E*)-C_6H_5CH=CHCH(OH)CH_3, 81176-43-4; (*R*)-(*E*)-C_6H_5CH=CHCH(OH)CH_3, 62413-47-2; (*S*)-(*E*)-CH_3CH=CHCH(OH)CH_3, 926-58-9; (*R*)-(*E*)-CH_3CH=CHCH(OH)CH_3, 35666-69-4; (*S*)-$(CH_3)_2C$=CHCH(OH)CH_3, 50373-46-1; (*R*)-$(CH_3)_2C$=CHCH(OH)CH_3, 74112-34-8; (*S*)-(*E*)-$CH_3(CH_2)_6CH$=CHCH(OH)CH_3, 95586-07-5; (*R*)-(*E*)-$CH_3(CH_2)_6CH$=CHCH(OH)CH_3, 95586-08-6; imidazole, 288-32-4.

Conformational Analysis of 1,3-Dioxacycloheptanes. 5. Conformations of 4-Isopropyl-3,5-dioxabicyclo[5.*n*.0]alkanes

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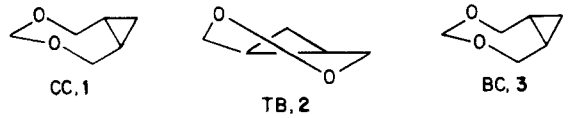
Received October 2, 1984

Interest in twist conformations of the 1,3-dioxacycloheptanes[1,2] has led to an investigation of the effect that three-membered rings have on the conformations of these compounds. Previous studies have shown that low barriers in the pseudorotation process make conformational analysis of these compounds difficult and that construction of a three-membered ring[3] or a double bond[4] at C_5–C_6 is sufficient to stop the pseudorotation process. The 3,5-dioxabicyclo[5.1.0]octanes[3] have well-defined boat–chair (BC), chair–chair (CC), and twist-boat (TB) conformations.



NMR data indicate that *exo*- and *endo*-4-isopropyl-3,5-dioxabicyclo[5.1.0]octanes prefer the CC **4** and BC **5** conformations, respectively. In contrast, *endo*- and *exo*-4-isopropyl-3,5,8-trioxabicyclo[5.1.0]octanes prefer the TB conformations **6** and **7**, respectively.[3,5]

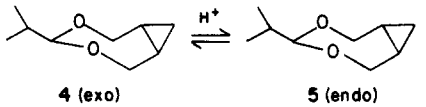
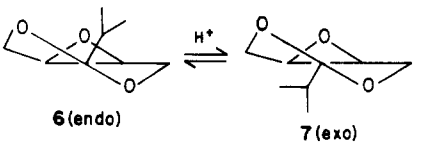


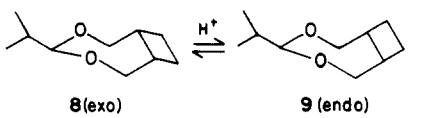
Table I. Equilibrium Data for *endo*/*exo*-4-Isopropyl-8,8-dichloro-3,5-dioxabicyclo[5.1.0]octane

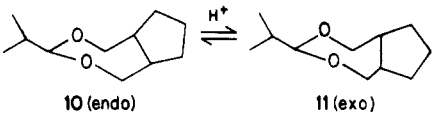
endo ⇌ exo

T, K	*K*	−Δ *G*°, kcal/mol	−Δ*H*°, kcal/mol	−Δ*S*°, gibbs
298	3.36 ± 0.15	0.72	1.62	3.0
323	2.60 ± 0.14	0.61		
348	2.27 ± 0.12	0.57		



We have extended these studies to include four- and five-membered rings and now report that *exo*- and *endo*-4-isopropyl-3,5-dioxabicyclo[5.2.0]nonanes prefer the CC **8** and BC **9** conformations, respectively. The five-membered ring homologues *exo*- and *endo*-4-isopropyl-3,5-dioxabicyclo[5.3.0] decanes prefer CC **11** and BC **10** conformations, respectively. The NMR spectra indicate that each of these conformations is well-defined, and we conclude that even the five-membered ring raises the torsional energy about the C_1–C_7 bond sufficiently high to stop the pseudorotational process in the CC and BC conformations.





A recent report that 8,8-dichloro-3,5-dioxabicyclo-[5.1.0]octane exists preferentially in the CC conformation is of special interest.[6] Models indicate that the endo (BC) of 4-isopropyl-8,8-dichloro-3,5-dioxabicyclo[5.1.0]octane has a chlorine atom proximate to the oxygen atoms in the ring. This would create a dipole–dipole interaction which the molecule can avoid by assuming a TB conformation. The alternative is to ring flip but that would put the isopropyl group in an axial position which is conformationally intolerable. To test the effect of such a dipole–dipole interaction the *endo*- **12** and *exo*-**13** isomers were synthesized by the addition of dichlorocarbene to 2-isopropyl-1,3-dioxacyclohept-5-ene. The NMR spectrum of the endo isomer is consistent with a TB conformation while the NMR spectrum of the exo isomer indicates that a CC conformation is preferred. It is interesting to note that the endo and exo epoxides **6** and **7** each prefer a TB conformation in solution. However, X-ray[8] data indicate that

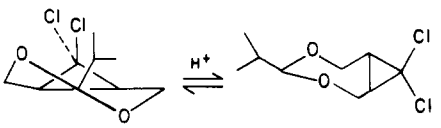


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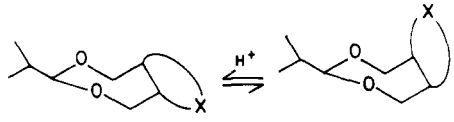
Table II. Thermodynamic Parameters for the Twist to Chair Equilibrium K_{eq} = (Twist)/(Chair)

	$-\Delta G°$, kcal/mol	$-\Delta H°$, kcal/mol	$-\Delta S°$, gibbs	ref
cyclohexane	4.9	5.9	3.5	14c
1,3-dioxacyclohexane	8.0	8.6	2.2	14a,b
1,3-dithiacyclohexane	2.7	4.3	4.7	14a,b
8,8-dichloro-3,5-dioxabicyclo[5.1.0]octane	0.72	1.6	3.0	

Table III. Conformational Free Energies for 4-Isopropyl-3,5-dioxabicyclo[5.*n*.0]alkanes



X	K ($DCCl_3$)	$\Delta G°_{298}$, kcal/mol
$-CH_2-$	1.22 ± 0.10	−0.12
$-CH_2CH_2-$	1.15 ± 0.11	−0.08
$-CH_2CH_2CH_2-$	0.81 ± 0.12	+0.12
$-CCl_2-$	0.30 ± 0.15	+0.72

3,5,8-trioxabicyclo[5.1.0]octane prefers a BC conformation analogous to **5**. Therefore the O_3–O_8 and O_5–O_8 dipole–dipole oxygen interactions are not so severe in the solid as to cause a ring flip to a CC conformation or TB conformation.

The stabilization of the TB conformations **6** and **7** has been attributed to the anomeric effect,[3,7] that is, the gauche O–C–C–O conformation is prefered over the syn or anti peri-planar conformations. If the anomeric effect was responsible for the TB conformation **12**, then **13** should have also been in a TB conformation. This suggests that a dipole–dipole interaction plays little or no part in the conformation of these compounds.

Equilibration Studies. A study of the *endo*/*exo*-4-isopropyl-8,8-dichlorodioxabicyclo[5.1.0]octane equilibrium as a function of temperature gave the data in Table I. The enthalpy differences between the TB and CC is 1.6 kcal/mol, and the entropy difference is 3.0 Gibbs. The enthalpy difference is considerably smaller than those for corresponding TB–C equilibria in six-membered rings (Table II). The entropy value reflects the mobility of the TB conformation.

An estimate of the dipole–dipole repulsion energy is possible if the assumption is made that conformations **13** and **14** differ in energy only in a 1–3 Cl–H interaction due to the endo chlorine atom in **13**. Models indicate that the distance between the endo chlorine and the C2 axial hydrogen in **13** is very close to the 1–3 axial–axial distance for *cis*-4-*tert*-butyl-1-chlorocyclohexane. The A value for this interaction is 0.53 kcal/mol.[9] Equilibration of *endo*/*exo*-4-isopropyl-3,5-dioxabicyclo(5.1.0)octane gave $\Delta G°_{298}$ of +0.12 kcal/mol (Table III). The estimated dipole–dipole repulsion energy is (0.72 − 0.53) + 0.12 = 0.31 kcal/mol.

The data from Table III show that the equilibrium changes from a preferred endo configuration to a preferred exo configuration as *n* increases from 1 to 3. Models indicate that the C_2 and C_8 axial hydrogens for **4** are eclipsed and are somewhat closer than the corresponding hydrogens for **11**. In addition, in **4** one axial hydrogen has two such interactions (on C_2 and C_6) whereas **11** has two separate interactions; C_2 and C_{10}, C_6 and C_8.

The C_2 and C_{10} axial hydrogens for **11** are staggered and represent a less energetic 1,3 H–H interaction than for an eclipsed orientation. In addition the five-membered ring can pucker to aid in the relief of strain. Accordingly, the $\Delta G°$ values appear to reflect the relative energies of the exo isomers.

^{1}H NMR Studies. All configurational assignments were made on the basis of the coupling constants for the C_1 and C_2 hydrogens and the chemical shift for the C_4 hydrogen. The axial and equatorial hydrogens were assigned by comparison with known spectra of similar bicyclo[5.1.0]-alkane systems.[1,6] Like the cyclohexanes the equatorial hydrogen for these exo isomers gives signals at a lower field than the corresponding axial hydrogen. However, the chemical shifts for the endo isomer do not follow the pattern. The signal for the C_2 axial hydrogen is downfield from that of the C_2 equatorial hydrogen. The small ring shields the C_2 axial hydrogen less in the endo isomer than in the exo isomer because the C_2 axial hydrogen lies more in the face of the ring in the exo isomer. The chemical shifts for the C_4 axial hydrogens for the endo isomers are downfield from the chemical shifts of the corresponding axial hydrogen of the exo isomers.[3] The coupling constants were readily ascertained from the 250-MHz spectra, and these portions of the spectra were clearly AMX. Spectra were duplicated by using a LAOCOON III program.

Conformational assignments were made from the coupling constants (reported in hertz) of the C_1 and C_2 hydrogens. The coupling constants are consistent with dihedral angles measured from models. The isopropyl group is an effective conformational bias, and there was no evidence of pseudorotation except for the TB conformations.

***endo*- and *exo*-4-Isopropyl-3,5-dioxabicyclo[5.3.0]-decane.** The endo and exo isomers were separated by GLC. The first peak was the exo isomer and gave coupling constant of J_{2a-1a} = 10.37, J_{2a-2e} = −12.1, and J_{2e-1a} = 4.70 Hz, and the chemical shift for the C_4 axial hydrogen was 4.17 ppm. The coupling constants are consistent with a CC conformation. The 2a–1a value reflects the large diehdral angle for this conformation while the 2e–1a value is consistent with a dihedral angle of approximately 60°. The endo isomer gave coupling constants of J_{2a-1e} = 2.39, J_{2e-1e} = 3.50, and J_{2a-2e} = −12.66 Hz, and the C_4 axial hydrogen gave a signal at 4.13 ppm.

***endo*- and *exo*-4-Isopropyl-3,5-dioxabicyclo[5.2.0]-nonane.** The endo and exo isomers were separated by GLC. The first peak gave coupling constants of J_{2a-1e} = 2.0, J_{2e-1e} = 1.0, and J_{2a-2e} = −13.0 Hz while the C_4 axial hydrogen had a chemical shift of 4.03 ppm. These values are consistent with an endo configuration and a BC conformation.

The exo isomer gave coupling constants of J_{2a-1a} = 11.1, J_{2e-1a} = 6.7, and J_{2a-2e} = −12.7 Hz while the signal for the C_4 axial hydrogen was 4.19 ppm. These values are similar to those for compound **4** and are consistent with a CC conformation.

***endo*- and *exo*-4-Isopropyl-8,8-dichloro-3,5-dioxabicyclo[5.1.0]octanes.** The endo isomer gave an ABXX′ spectrum[11] with coupling constants for the C_1 and C_2 hydrogens of J_{2a-1e} = 6.31, J_{2e-1e} = 5.43, and J_{2a-2e} = −13.5 Hz. This spectrum is very much like that of *exo*-8-bromo-4,4-dimethyl-3,5-dioxabicyclo[5.1.0]octane which is reported to exist in a TB conformation.[6] These coupling constants are in marked contrast to *endo*-4-isopropyl-3,5-dioxabicyclo[5.1.0]octane (**5**) which has values of J_{2a-1e} = 1.3 and J_{2e-1e} = 0.12 Hz and exists in a BC conformation.

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The ^{13}C chemical shifts of **12** are also consistent with this assignment. The C_2 chemical shift for the endo isomer is 62.33 ppm and 70.06 ppm for the exo isomer. These compare with values of 73.66 and 72.88 ppm for the corresponding carbons of *endo*- and *exo*-4-isopropyl-3,5-dioxabicyclo(5.1.0)octanes, **4** and **5**, respectively. This is consistent with the Gorenstein interpretation of the γ *effect*, that is, the γ *effect* is a function of the dihedral angle between the carbon in question and the γ-carbon.[10] For the exo isomer **13** the orientation between C_2 and the methine (CH) carbon of the isopropyl group is anti whereas for the endo isomer **12** it is gauche. Accordingly the endo isomer gives a C_2 resonance upfield from the exo isomer **13**. The C_2 chemical shifts for **4** and **5** are nearly the same because they have the same anti orientations to the isopropyl methine carbons.

The exo isomer **13** gave coupling constants of J_{2a-1a} = 9.56, J_{2e-1a} = 7.34, and J_{2a-2e} = −13.45 Hz. These values are consistent with values reported for *exo*-4-phenyl-8,8-dichloro-3,5-dioxabicyclo[5.1.0]octane[12] which is known to exist in a CC conformation.

Experimental Section

NMR spectra were recorded on a Brücker 250 spectrometer. Samples were run in deuterochloroform as 10% solutions. All chemical shifts are reported in parts per million downfield from internal Me_4Si. Spectra were reproduced by LAOCOON III. The ^{13}C NMR spectra were recorded at 25.15 MHz on a Varian HA-100D spectrometer. All chemical shifts are reported in parts per million downfield from interal Me_4Si. All mass spectra were determined on a AE1-9 high-resolution spectrometer. Equilibration were run in deuteriochloroform at 25 °C unless otherwise noted, and equilibrium was approached from both sides using samples enriched in one isomer. Amberlite IR-120 (plus) was used as the catalyst.

cis-1,2-Bis(hydroxymethyl)cyclopentane[13] and 2-isopropyl-1,3-dioxacyclohept-5-ene[3] were synthesized as described in the literature. *cis*-1,2-Bis(hydroxymethyl)cyclobutane was prepared by $LiAlH_4$ reduction of *cis*-1,2-cyclobutanedicarboxylic anhydride and used without further purification.

***endo*- and *exo*-4-Isopropyl-3,5-dioxabicyclo[5.2.0]decane.** The general procedure for the preparation of these compounds has been described previously.[1,3] The mixture of endo and exo isomers was prepared in 73% yield by the reaction of isobutyraldehyde and *cis*-1,2-bis(hydroxymethyl)cyclopentane, bp 80–85 °C (20 torr). The isomers were separated by GLC (8 ft 10% polyphen, Chromosorb W), and the endo isomer was the first peak: ^1H NMR $CH_a(4)$ δ 4.13, $CH_a(2)$ 3.88, $CH_e(2)$ 3.66, $CH_e(1)$ 2.11, CH_2(ring) broad multiplet at δ 1.7, CH(isopropyl) 1.90, CH_3 0.92. The exo isomer was the second peak: ^1H NMR $CH_a(4)$ δ 4.17, $CH_a(2)$ 3.49, $CH_e(2)$ 3.91, $CH_a(1)$ 3.48, CH(isopropyl) 1.80, CH_3 0.93. A mass spectrum gave m/e 141 (parent minus isopropyl).

***endo*- and *exo*-4-Isopropyl-8,8-dichloro-3,5-dioxabicyclo-[5.1.0]octane.** The synthetic procedure used to synthesize these compounds is the same as described in reference[6] except that 2-isopropyl-1,3-dioxacyclohept-5-ene was used as the olefin. The mixture of endo and exo isomers was prepared in 30% yield. The fraction boiling at 92–95 °C (3 torr) was collected and separated by GLC (8ft Carbowax 20 M, 15% on Chromosorb W). The exo isomer was the first peak: ^1H NMR $CH_a(4)$ δ 4.30, $CH_a(2)$ 3.80, $CH_e(2)$ 4.67, $CH_a(1)$ 2.38, CH(isopropyl) 1.88, C(methyl) 0.98; ^{13}C NMR $C_{(1,7)}$ δ 35.03, $C_{(2,6)}$ 70.06, $C_{(4)}$ 116.0, $C_{(8)}$ 97.63, C(isopropyl) 33.40, C(methyl) 18.24; mass spectrum m/e 225 (parent peak).

The endo isomer was the second peak: ^1H NMR $CH_a(4)$ δ 4.35, $CH_a(2)$ 4.08 (or 4.15) $CH_e(2)$ 4.15 (or 4.08), $CH_a(1)$ 2.02, CH(isopropyl) 1.75, CH_3 0.87; ^{13}C NMR C(1,7) δ 33.59, C(2,6) 62.33, C(4) 108.48, C(isopropyl) 32.73, C(methyl) 17.31; mass spectrum, m/e 225 (parent peak).

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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A Mass Spectrometry Study of Levoglucosenone

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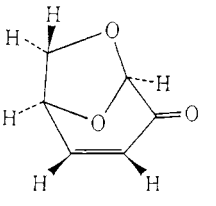
Received September 24, 1984

Levoglucosenone has attracted the attention of researchers the world over. Even though its structure is known,[1] no satisfactory determination of its molecular weight has been reported. The compound was reported by Tsuchiya and Sumi[2] as the major constituent of the tar fraction from the pyrolysis of acid-treated cellulose. Woodley[3] reported it as a major compound in the tar fraction from the pyrolysis of both cellulose and levoglucosan. Originally the empirical formula $C_5H_6O_2$ was assigned to the compound on the basis of the appearance of m/z 98 in the mass spectra recorded. Lipska and McCasland,[4] on the basis of IR, MS, and NMR concluded the material to be 1,5-anhydro-2,3-dideoxy-β-D-pent-2-enofuranose. Lam et al.[5] identified the material as *cis*-4,5-epoxy-2-pentanal. In 1973, however, Halpern, Riffer, and Broido[1] showed by carbon-13 NMR that the material was comprised of six carbon atoms. Therefore, the ion m/z 98, which was the primary reason for determination of the empirical formula $C_5H_6O_2$ by previous researchers, was now believed to be an ion resulting from fragmentation of the molecular ion. Halpern et al.[1] identified the compound as 1,6-anhydro-3,4-dideoxy-Δ^3-β-D-pyranosen-2-one (1). This has been accepted as the correct structure for levoglucosenone.



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The role of levoglucosenone in the pyrolysis of cellulose in relation to the fire retardancy of cellulosic materials, as well as its physical and chemical properties, have been studied extensively.[6-19] Determination of the correct

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