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Carbon-13 Nuclear Magnetic Resonance. Conformation in Some 1,3-Dioxacycloheptanes

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The carbon-13 nuclear magnetic resonance chemical shifts for some 1,3-dioxacycloheptanes are reported. The chemical shifts for the ring carbons are affected by the positions and conformations of the substituents. Substituent shift parameters can be transferred from 1,3-dioxanes and cycloheptanes to 1,3-dioxacycloheptanes. Bulky substituents in the 2, 4, and 7 positions of the 1,3-dioxacycloheptanes do little to reduce the number of available low-energy conformations.

Carbon-13 nuclear magnetic resonance is a potent tool for conformational analysis because carbon-13 chemical shift substituent parameters reflect both substituent and conformational effects. Appropriate substituent parameters can be obtained not only in cyclohexanes,[3] but also in cycloheptanes[4] and 1,3-dioxanes,[5] provided that the effects of oxygen substitution in the six-membered ring and of pseudo-rotation of the seven-membered ring are taken into account.

Encouraged by previous work,[3-5] we undertook a study of carbon-13 substituent effects in some 1,3-dioxacycloheptanes in an effort to extend the correlations to this ring system and to provide a basis for conformational assignment therein.

Conformational analysis of cyclohexane[6] and 1,3-dioxane[5] is facilitated by the absence of a low-energy pseudorotational barrier and the availability of only one low-energy conformation. The interpretation of conformational data for cyclopentanes,[7] 1,3-dioxolanes,[8] cycloheptanes,[4] and 1,3-dioxacycloheptane[1b] is made more difficult by the availability of numerous low-energy conformations and by the low-energy pseudo-rotational barriers for each of these compounds, with the result that in these systems one must think in terms of conformational arrays.

The geometry of 1,3-dioxacycloheptane has been discussed previously and comparisons were made with cyclohexanes, cycloheptanes, and 1,3-dioxanes:[1b] there are four distinct chair conformations for 1,3-dioxacycloheptane compared to one for each of the other compounds; the 1,3-COC distance is small owing to the shorter carbon–oxygen bond (compared to the CCC distance); 1,3-diaxial Me–H interactions are more severe (as in the 1,3-dioxanes)[9,10] than in cyclohexane and cycloheptane;[10] and the 4,7-diaxial Me–H interaction is more severe than that in cycloheptane. Accordingly, an additional objective of these studies was to test whether these more severe interactions could be used to advantage to produce compounds with only one or two low-energy conformations in the conformational array. Therefore the synthesis of 1,3-dioxacycloheptanes with a number of bulky substituents properly located to take advantage of the decreased 1,3-diaxial and 4,7-diaxial distances was undertaken.

The carbon-13 spectra were recorded at ambient temperatures at which the rates of interconversions of the conformations were fast. Therefore the chemical shifts are average values to which each of the conformations contributes according to its population.

The carbon-13 chemical shifts for a series of 1,3-dioxacycloheptanes are summarized in Table I. The assignments of the carbon-13 resonances were made on the basis of relative intensities, comparisons with chemical shifts for 1,3-dioxanes,[5,11] and comparison with values for 1,3-dioxacyclohept-5-ene.[1]

The chemical shift assignments are reasonably straightforward. The *tert*-butyl methyl carbons were readily distinguished from methyl groups substituted directly on the ring by signal intensity. The signal of the quaternary carbon of the *tert*-butyl group was distinguished from those for C_5 and C_6 by its reduced intensity.[12] The chemical shifts for C_5 and C_6 were readily assigned, since they were the only ones without parallel in the spectrum of 1,3-dioxacyclohept-5-ene. The signals assigned to C_2, C_4, and C_7 correspond to the chemical shifts for C_2, C_4, and C_6 in 1,3-dioxanes.

Some important generalizations may be drawn from Table I. The difference in geometry between a seven- and

Table I
Carbon-13 Chemical Shifts for Some 1,3-Dioxacycloheptanes[a]

Entry	Compd	C_2	C_4	C_7	C_5	C_6	$2C_c$[b]	Bu_{Me}	Me
I	1,3-Dioxacycloheptane	94.67	67.24		30.05				
		(96.77)	(68.71)		(27.95)				
II	*cis*-4,7-Dimethyl-	94.07	75.89		33.76				22.36
III	*trans*-4,7-Dimethyl	91.95	72.39		36.51				22.58
IV	*cis*-2-*t*-Butyl 4-methyl-	108.70	76.98	70.68	36.70	28.31	36.64	25.10	22.32
		(107.26)	(72.49)		(33.69)		(35.06)	(24.95)	(21.92)
V	*trans*-2-*t*-Butyl-4-methyl-	106.39	71.23	66.87	36.64	29.50	36.21	25.36	22.32
VI	*r*-2-*tert*-Butyl-*cis*-4,*cis*-7-dimethyl-	108.88	75.12		33.79		35.72	25.10	22.65
VII	*r*-2-*tert*-Butyl-*cis*-4,*trans*-7-dimethyl-	105.60	70.54	77.90	36.64		35.90	25.24	22.65
VIII	5,5-Dimethyl-	94.64	75.93	63.05	34.68	44.15			25.73
		(96.22)	(79.10)		(31.71)				(23.20)
IX	2-*tert*-Butyl-5,5-dimethyl-	110.24	78.47	64.14	36.68	43.67	35.05	24.82	25.33, 25.08
		(108.41)	(77.31)		(30.13)		(34.99)	(25.17)	(23.36, 22.18)
X	4-Methyl-	93.50	75.32	66.80	36.93	29.29			22.51
XI	5-Methyl-	94.65	72.40	64.84	34.95	38.44			17.27
XII	2-*tert*-Butyl-	109.94	68.70		29.71		36.51	25.21	
		(107.83)	(66.92)		(26.37)		(35.23)	(25.01)	

[a] All values are in parts per million downfield from internal TMS. Parenthetical values are from ref 5. [b] The quaternary carbon of the *tert*-butyl group.

six-membered ring has little effect on the chemical shifts of the ring carbons. The chemical shifts of 1,3-dioxane and 1,3-dioxacycloheptane differ by not more than 3 ppm. Those for substituent groups are within ±2 ppm.

The chemical shifts of the quarternary carbon of the *tert*-butyl group are remarkably constant and give no indication of a major contribution from an axially oriented *tert*-butyl group. The same conclusion is drawn from the narrow range of the chemical shifts for the methyl carbon of the *tert*-butyl group. A steric compression at the methyl carbon of the *tert*-butyl group must result in a paramagnetic shift for that carbon as well as for the particular ring or substituent carbon. There is no indication of any major paramagnetic shift for the *tert*-butyl carbons; thus conformations with axial *tert*-butyl groups are excluded.[5]

Contrary to the reports for the cyclohexanes and the 1,3-dioxanes, the chemical shifts for the substituent methyl groups do not indicate a conformational preference. This is certainly due to conformational averaging; for example, there are two methyl absorptions for 2-*tert*-butyl-5,5-dimethyl-1,3-dioxacycloheptane but chemical shift difference is only 0.2 ppm. The difference between the chemical shift for an axial and equatorial methyl carbon is greater than 1 ppm for the 1,3-dioxanes and 3 ppm for the cyclohexanes.

Configurational Assignments. Configurations for entries II–V have been previously established.[1b] The 2,5-hexanediol which was used for the preparation of *cis*-4,7-dimethyl-1,3-dioxacycloheptane and *trans*-4,7-dimethyl-1,3-dioxacycloheptane was shown to contain 80% of the meso iosmer and 20% racemate. The meso diol gave the cis isomer and the racemate gave the trans isomer.[1b] The meso diol also gave the *r*-2-*tert*-butyl-*cis*-4,*cis*-7-dimethyl-1,3-dioxacycloheptane in reaction with trimethylacetaldehyde while the racemic diol gave the *r*-2-*tert*-butyl-*cis*-4,*trans*-7-dimethyl-1,3-dioxacycloheptane.[13] The proton magnetic resonance spectra are consistent with this assignment. The cis-4,trans-7 isomer has absorptions at τ 6.43 and 6.04 for the protons on C_4 and C_7, consistent with nonequivalency at these positions, while the cis-4,cis-7 isomer had only one absorption at τ 6.21. In addition the C_2 proton absorption of the cis-4,trans-7 isomer is at lower field, τ 5.74, than that of the cis-4,cis-7 isomer, τ 5.92. This is consistent with the data for *cis*-2-*tert*-butyl-4-methyl-1,3-dioxacycloheptane (τ 5.89) and *trans*-2-*tert*-butyl-4-methyl-1,3-dioxacycloheptane (τ 5.83). The carbon-13 data are also consistent with these assignments. The carbon-13 chemical shift of C_2 in *r*-2-*tert*-butyl-*cis*-4,*trans*-7-dimethyl-1,3-dioxacycloheptane is 3.3 ppm upfield from the same absorption for the cis-4,cis-7 isomer. This is consistent with a 1,3-Me–H interaction at C_2 for the cis-4,trans-7 isomer. There are no conformations for the cis-4,cis-7 isomer in which the methyl groups contribute a paramagnetic[3] shift at C_2. In addition the cis-4,trans-7 isomer gives different chemical shifts for C_4 (70.54) and Ci7 (77.90), which is consistent with the proton nmr data, while the cis-4,cis-7 isomer has only one absorption for C_4 and C_7 (75.12 ppm) indicating equivalency for these positions.[15]

Conformational Assignments. Table II lists the carbon-13 chemical shift substituent effects produced by substitution on 1,3-dioxacycloheptane. Table III summarizes these same effects but lists them as to their origin, *i.e.*, α, β, γ, δ, and also lists substituent effects produced by substitution in 2-*tert*-butyl-1,3-dioxacycloheptane and 4-methyl-1,3-dioxacycloheptane. The values in brackets are from corresponding cycloheptanes and the values in parentheses are from corresponding 1,3-dioxanes.

The α and β effects are consistent with those for cyclohexane, cycloheptane, and 1,3-dioxane. The correlation in the direction (sign) of these substituent effects is excellent but the magnitude of the values shows some variation. The α effect of −8.08 ppm for a 4-methyl substituent compares favorably with −6.7 ppm for methylcycloheptane and −5.96 ppm for methylcyclohexane. The β effect of −6.88 ppm is also reasonable when compared to −9.3 ppm for methylcycloheptane and −9.03 ppm for methylcyclohexane. The values for the 5-methyl substituent agree somewhat more closely.

Substitution of a geminal dimethyl group gives α values of −4.63, −3.76, −5.1, and −3.1 ppm for 5,5-dimethyl-1,3-dioxacycloheptane, 5,5-dimethyl-1,3-dioxane, 1,1-dimethylcycloheptane, and 1,1-dimethylcyclohexane, respectively. The β effects are −8.69 (−14.10), −10.39, −14.4, and −12.7 ppm for the same sequence. The α and β effects are in remarkably good agreement. The change in geometry and substitution of two oxygen atoms in the ring does not prohibit the use of these parameters for the assignment of chemical shifts. Their utility in the assignment of conformation, however, appears questionable. No clear correlation with the degree of axial substitution is apparent. The γ and δ effects do however, appear to corre-

Table II
Carbon-13 Chemical Shift Substitutent Effects for Some 1,3-Dioxacycloheptanes[a,b]

Entry	Compd	C(2)	C(4)	C(5)	C(6)	C(7)
1	4-Methyl-	+1.17	−8.08	−6.88	+0.76	+0.44
2	5-Methyl-	+0.02	−5.16	−4.90	−8.39	+2.40
3	*cis*-4,7-Dimethyl-	+0.60 (+0.7)	−8.65 (−4.9)	−3.71 (−14.0)	−3.71	−8.65 (−4.9)
4	*trans*-4,7-Dimethyl-	+2.72 (+7.2)	−5.15 (−0.0)	−6.46 (−10.7)	−6.46	−5.15
5	5,5-Dimethyl-	+0.03	−8.69	−4.63	−14.10	+4.19
6	2-*tert*-Butyl-	−15.27	−1.46	+0.34	+0.34	−1.46
7	2-*tert*-Butyl-5,5-dimethyl-	−15.57	−11.23	−6.63	−13.62	+3.10
8	*cis*-2-*tert*-Butyl-4-methyl-	−14.03	−9.74	−6.65	+1.74	−3.44
9	*trans*-2-*tert*-Butyl-4-methyl-	−11.72	−3.99	−6.59	+0.55	+0.37
10	*r*-2-*tert*-Butyl-*cis*-4,*cis*-7-dimethyl-	−14.21	−7.88	−3.74	−3.74	−7.88
11	*r*-2-*tert*-Butyl-*cis*-4,*trans*-7-dimethyl-	−10.93	−3.30	−6.59	−6.59	−10.66

[a] All values are in parts per million calculated from 1,3-dioxacycloheptane. [b] Values in parentheses are for the corresponding 1,3-dioxanes from ref 11. A negative value indicates a signal downfield from the reference carbon.

Table III
Carbon-13 Chemical Shift Substituent Effects Produced by Substitution on 1,3-Dioxacycloheptane,[a] 4-Methyl-1,3-dioxacycloheptane,[b] and 2-*tert*-Butyl-1,3-dioxacycloheptane[c]

Compd	α	β	γ	δ
4-Methyl-[a]	−8.08 [−6.7][d]	−6.88 [−9.3]	1.17, −0.76 [1.3]	0.44 [−0.7]
5-Methyl-[a]	−4.90	−5.16, −8.39	2.40	0.02
2-*tert*-Butyl-[a]	−15.27 (−11.06)[e]		−1.46 (1.79)	0.34 (1.58)
5,5-Dimethyl-[a]	−4.63 (−3.76) [−5.1]	−8.69, −14.10 (−10.39) [−14.4]	4.19 [4.4]	0.03 (0.55) [−2.6]
cis-4,7-Dimethyl-[b]	−9.09 [−5.3]	−4.47 [−6.6, −9.5]	3.17, −0.57 [4.0, −0.1]	−2.57 [0.7, −0.9]
trans-4,7-Dimethyl-[b]	−5.59 [−6.3]	−7.22 [−9.7 or −7.9]	0.42, 1.55 [2.8, 0.9]	2.93 [0.7, −0.3]
2-*tert*-Butyl-5,5-dimethyl-[c]	−6.97 (−3.76)	−9.77, −13.96 (−10.39)	4.56	−0.30 (−0.58)
cis-2-*tert*-Butyl-4-methyl-[c]	−8.28 (−5.55)	−7.00 (−7.32)	1.40, 1.24 (0.51, 0.57)	−1.98
trans-2-*tert*-Butyl-4-methyl-[c]	−2.56	−7.14	0.21, 3.55	1.93
r-2-*tert*-Butyl-*cis*-4,*cis*-7-dimethyl	−6.42	−4.08	1.06	
r-2-*tert*-Butyl-*cis*-4,*trans*-7-dimethyl-[c]	−1.84, −9.20	−6.93	4.34	

[a] Taken from chemical shifts compared to 1,3-dioxacycloheptane. [b] Chemical shifts compared to 4-methyl-1,3-dioxacycloheptane. [c] Chemical shifts compared to 2-*tert*-butyl-1,3-dioxacycloheptane. [d] Values for cycloheptanes taken from ref 4. [e] Values for 1,3-dioxanes taken from ref 5.

late with the degree of axial character in a conformational array.

The relation of the γ effect to conformation is probably the best understood of the chemical shift substituent parameters.[3,5,7] It reflects a paramagnetic shift due to a 1,3-diaxial steric compression. The δ effects reflect the same type of interaction for the 4,7-diaxial compression found in cycloheptanes and 1,3-dioxacycloheptanes.

The γ shift substituent parameter indicates that there are more conformations with axial-like methyl groups for the cis isomer of 4,7-dimethyl-1,3-dioxacycloheptane than there are for the trans isomer. It is also evident that *trans*-2-*tert*-butyl-4-methyl- and *r*-2-*tert*-butyl-*cis*-4,*trans*-7-dimethyl-1,3-dioxacycloheptane have a higher population of methyl axial conformers than the corresponding cis isomers.

It is evident from the data that the chemical shifts and the substituent shift parameters parallel those found for other systems. As expected, the data for the substituted 1,3-dioxacycloheptanes studied here fail to indicate the presence of a single, highly populous conformation. The data are capable of signaling the presence of conformations with axial-like methyl groups and the absence of conformations with axial-like *tert*-butyl groups but do not indicate the total conformational picture.

Experimental Section

Proton nmr spectra were recovered on a Varian A-60A instrument. Samples were run as 10% solutions in carbon tetrachloride. All chemical shifts are reported in τ units. The carbon-13 nmr spectra were recorded at 25.15 MHz on a HA-100D nmr spectrometer interfaced to a Digilab NMR-FTS-3 pulse and data system. The samples were neat liquids. The number of data points was 8*K* or 16*K* as required to obtain satisfactory resolution. Spectra were recorded with broad-band decoupling. All chemical shifts were referenced to internal TMS and reported in parts per million. All m/e values were determined on a AEI MS-9 high-resolution mass spectrometer. Separations were carried out on a Hewlett-Packard F & M 5752 gas chromatograph. The infrared spectra were recorded on a Beckman IR-8 instrument and the absorption values are reported in microns.

The preparation of 1,3-dioxacycloheptane, 4,7-dimethyl-1,3-dioxacycloheptane, 2-*tert*-butyl-4-methyl-1,3-dioxacycloheptane, 4-methyl-1,3-dioxacycloheptane, and 5-methyl-1,3-dioxacycloheptane were previously described.[1]

2-*tert*-Butyl-1,3-dioxacycloheptane. The general procedure for the preparation of these compounds is that of Branncock and Lappin.[16] The preparation of 2-*tert*-butyl-1,3-dioxacycloheptane is described as a representative example. A mixture of 1.4 g (0.1 mol) of 1,4-butanediol, 8.6 g (0.1 mol) of pivaldehyde, 100 ml of benzene, and 50 mg of *p*-toluenesulfonic acid was refluxed using a Dean-Stark distillation trap. The reaction was terminated when 1.5 ml of water was evolved. The mixture was distilled under vacuum to give a 74% yield of the desired product: bp 28–30° (0.1

Torr); ir (neat) 3.23, 3.33, 6.56, 6.76, 8.22, and 9.30 μ; proton nmr (CCl_4) τ 5.96 (HC_2), 6.31 ($HC_{4,7}$), 8.51 ($HC_{5,6}$); m/e 101 (parent − *tert*-butyl).

2-*tert*-Butyl-4,7-dimethyl-1,3-dioxacycloheptane. The mixture of isomers distilled at 26° (0.3 Torr). The isomers were separated by glpc (8-ft 10% Apiezon-Chromosorb column) and the cis,cis isomer was the first peak: ir (neat) 3.38, 3.43, 3.50, 6.93, 8.78, 9.05 μ; proton nmr (CCl_4) τ 5.95 (HC_2), 6.21 (HC_7), 8.36 (HC_5, HC_6), 8.83 (CH_3), 9.12 (*tert*-butyl); m/e 130 (parent − *tert*-butyl). The cis,trans isomer was the second peak: proton nmr τ 5.94 (HC_2), 6.43 (HC_4), 6.04 (HC_7), 8.36 ($HC_{5,6}$), 8.86, 8.83 (CH_3), 9.12 (*tert*-butyl); m/e 130 (parent − *tert*-butyl).

5,5-Dimethyl-1,3-dioxacycloheptane. This compound was prepared in 75% yield from 2,2-dimethyl-1,4-butanediol and paraformaldehyde. The physical properties follow: bp 28° (0.3 Torr); proton nmr τ 5.28 (HC_2), 6.68 (HC_4), 6.31 (HC_7), 8.53 (HC_6), 9.10 (CH_3); m/e 130 (parent peak).

2-*tert*-Butyl-5,5-dimethyl-1,3-dioxacycloheptane. This compound was prepared in 57% yield from 2,2-dimethyl-1,4-butanediol and pivaldehyde: bp 22° (0.05 Torr); proton nmr τ 5.83 (HC_2), 6.30, 6.80 (HC_4, J = 11.5 Hz), 8.52 (HC_6), 9.02, 9.16 (CH_3), 9.12 (*tert*-butyl); m/e 186 (parent peak).

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Chemistry of the Sulfur–Nitrogen Bond. VII.[1] Rearrangement of Sulfenimines (*S*-Aryl Thiooximes) to β-Keto Sulfides. Attempted Synthesis of Benzo[*b*]thiophenes

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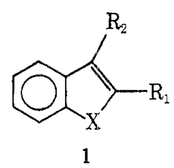
Attempts to rearrange sulfenimines **2** (X = S) to benzo[*b*]thiophenes are described. The major reaction is cleavage of the S–N bond. Sulfenimines in the presence of benzoyl chloride and 1,5-diazobicyclo[4.2.0]non-5-ene (DBN) rearrange to 2-benzamido-1-(arylthio)alkenes **11** and **13**. These compounds are readily hydrolyzed to β-keto sulfides. An intermolecular rearrangement involving a sulfenyl chloride is proposed to account for the formation of these products.

The synthesis of substituted indoles **1** (X = NH) involves a one-step rearrangement of the readily available phenylhydrazone **2** (X = NH). This rearrangement is known as the Fisher indole synthesis and is the primary synthetic route to these compounds.[3] Benzofurans **1** (X = O) have been prepared from the *O*-phenyl oxime ethers **2**



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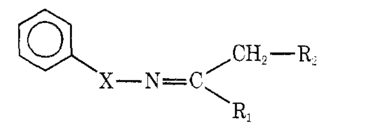


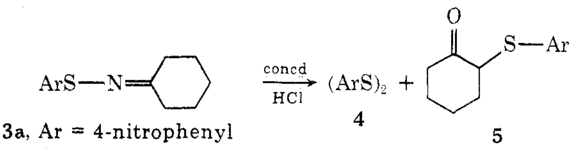
2

X = NH, O, S

(X = O).[4,5] These rearrangements are effected by heating the hydrazone or oxime ether in the presence of a Lewis acid or concentrated hydrochloric acid.[3-5] The rate-determining step is believed to involve a tautomerism of the hydrazone (or oxime ether) to the ene-hydrazine (ene-ether) followed by cyclization.[3,6]

The synthesis of substituted benzo[*b*]thiophenes **1** (X = S), however, generally involves multistep synthetic routes.[7] It would be convenient, therefore, if similar synthetic routes from the corresponding sulfenimines, **2** (X = S), were available for the synthesis of substituted benzo[*b*]thiophenes. Recently we reported a convenient one-step synthesis of sulfenimines, **2** (X = S), from silver nitrate, aromatic disulfides, ammonia and aldehydes, and ketones.[1,8]

Kaminsky, Shavel, and Meltzer reported an attempt to rearrange cyclohexanone sulfenimines **3a,b**, using concentrated hydrochloric acid, to the corresponding benzo[*b*]-



3a, Ar = 4-nitrophenyl
b, Ar = 2-pyridyl
c, Ar = 2-benzothiazole