^{17}O NMR Spectra of Tertiary Alcohols, Ethers, Sulfoxides and Sulfones in the Cyclohexyl and 5-Substituted 1,3-Dioxanyl Series and Related Compounds

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^{17}O NMR spectra of fifteen cyclohexane-derived tertiary alcohols and related ethers and acetals, six 1,3-dioxane-derived orthoesters, four cyclohexane- and 1,3-dioxane-derived sulfones and the four corresponding sulfoxides, three acyclic sulfones, six alcohols derived from norbornane and 1,3-dithiane and two esters have been recorded. Attention is drawn to δ-compression effects and saturation effects in several of these compounds.

INTRODUCTION

In a previous paper,[1] ^{17}O NMR spectra of several cyclohexanols and 1,3-dioxan-5-ols and their ethers were discussed. It was pointed out that axial alcohols and ethers resonate upfield of equatorial ones except when δ-compression effects[2] intervene, that the α-effect of methyl ether groups is upfield shifting and that a strong γ-*anti* effect[3] and a less strong γ-*gauche* effect lead to sizeable upfield shifts in the exocyclic oxygen resonances of the dioxanes, which are not reciprocated in the corresponding shifts of the ring oxygen in the equatorial isomer.

We have now investigated a number of additional alcohols, mostly tertiary, plus some ethers, acetals and orthoesters, shown in Schemes 1 and 2. Reference compounds from previous work[1,4,5] are included in each Scheme.

RESULTS AND DISCUSSION

Scheme 1 is concerned mainly with β-effects of various alkyl and aryl substituents. The following regularities can be observed (Table 1). (1) The β-effect in the ethers **8** and **9** is 12–15 ppm less than the corresponding effect in alcohols **6** and **7**. (2) The β-effect of equatorial methyl (in **7**), phenyl (in **11** and **12**) and ethinyl (in **17**) on the ^{17}O shifts of the alcohols is about the same (20–23 ppm) (a lesser effect is seen in the benzyl compound **15**, perhaps because of a counteracting γ-effect). (3) The situation is otherwise for axial substituents, where the β-effects are appreciably larger for the unsaturated groups. As a result, the differences between the axial and equatorial series are also largest for these substituents. It is of interest that a corresponding difference in γ-effects of the OH group is seen in the ^{13}C resonances of the *ortho* carbons of the phenyl rings, which are at 124.5 ppm for the equatorial and at 126.2 ppm for the axial phenyl.[6] While this might be a question of conformation (aryl ring perpendicular or parallel to the symmetry plane of the cyclohexane ring[7]) in the phenyl compounds, such an explanation cannot apply to the analogous ^{13}C shift differences of the β-carbons of the ethinyl derivatives (Table 2). The similarity of the chemical shift in **13** with that of **11**, and the large difference between **13** and **10** suggests that the phenyl group in **13** is nearly entirely equatorial, a conclusion in accord with a low-temperature ^{13}C NMR study.[9]

The difference between axial and equatorial β-effects is also seen in ^{13}C spectra. In methylcyclohexanes, equatorial methyl resonates at 23–24 ppm and axial methyl at 17.5–19.5.[10,11] The resonances of the geminal groups in 1,1,3-trimethylcyclohexane[10] are at 34.3 ppm (equatorial) and 25.5 ppm (axial). In the two conformers of 1-methyl-1-phenylcyclohexane, equatorial methyl resonates at 36.0 ppm and axial methyl at 24.0 ppm.[7b] It follows that the β-effect of equatorial methyl is 6–8 ppm and that of phenyl 4.5–6.5 ppm. For the axial substituents the effects are larger: methyl 10–11 ppm, phenyl 12–13 ppm (however, the difference between methyl and phenyl is very small).

Comparison of the ^{17}O chemical shifts of alcohols **6** and **7** with **8** and **9** indicates nearly the same α-effect of −45 to −47 ppm on introduction of the methyl ether group. This effect is substantially larger than that of −32 to −34 ppm in the secondary alcohol–ether pairs **1**, **2/3**, **4**. Similar differences between α-effects in secondary and tertiary alcohols have been noted earlier.[1]

The second set of compounds examined, consisting of ketals and orthoesters derived from cyclohexane and 1,3-dioxane, is shown, together with appropriate model compounds, in Scheme 2.

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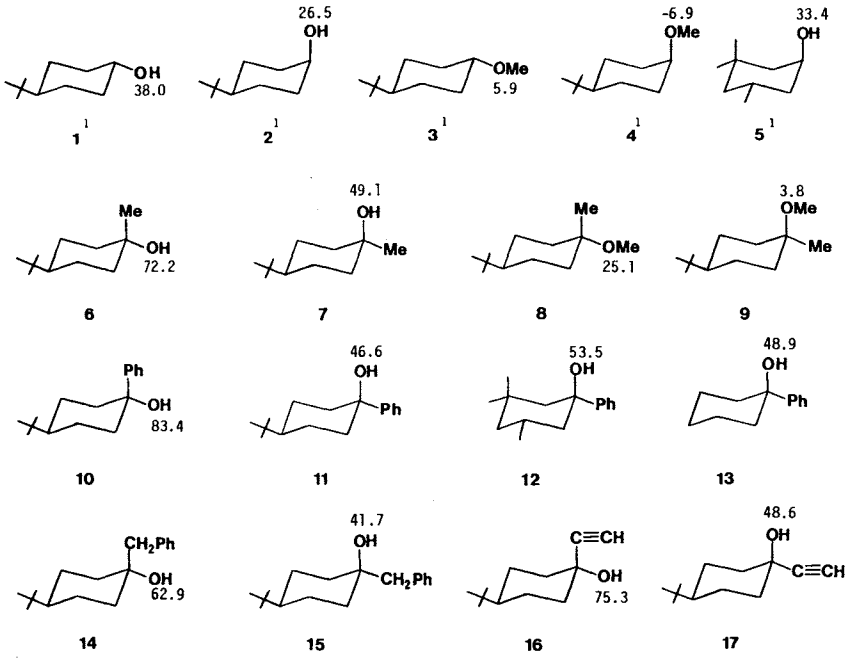
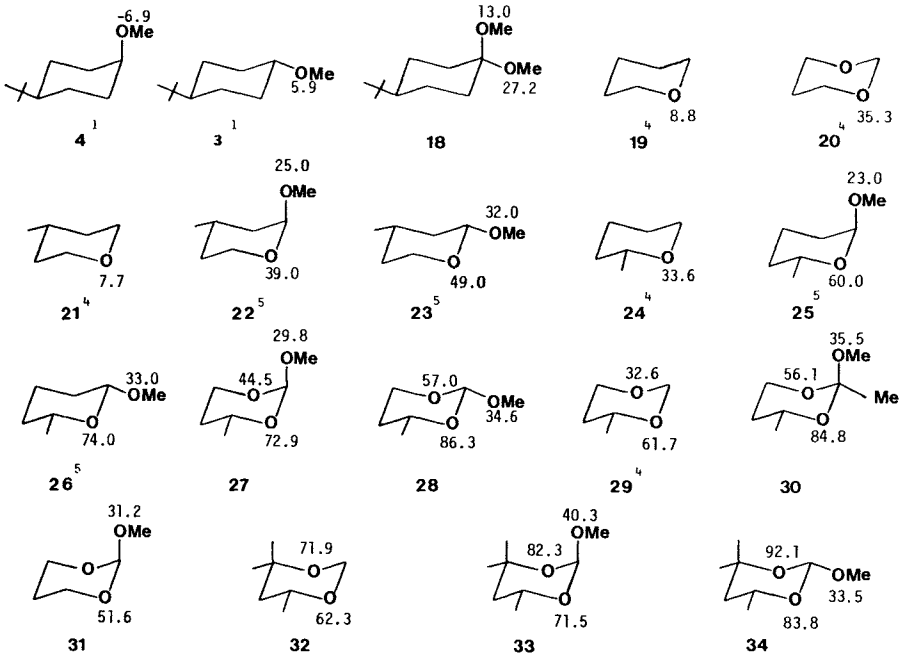


Scheme 1



Scheme 2

Table 1. β-Effects, ppm (downfield)

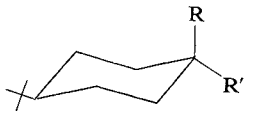
	Substituent					
	Me	Me (ether)	Ph	$PhCH_2$	HC≡C—	
Axial, compound	6	8	10	14	16	
Effect, ppm	34.2	19.2	45.4	24.9	37.3	
Equatorial, compound	7	9	11	15	17	12
Effect, ppm	22.6	10.7	20.1	15.2	22.1	20.1
Δ,[a] ppm	11.6	8.5	25.3	9.7	15.2	

[a] Difference between axial and equatorial substituent effects.

Compound **18** shows the expected difference between diastereotopic methoxy groups. The axial group presumably resonates upfield; the combined β- and γ-effects produced by the second methoxy substituent on the first are (by comparison with **4** and **3**) about the same (20–21 ppm) for both the equatorial and axial substituents. This is clearly different from the situation with a methyl substituent discussed above.

Comparison of oxane[4] (**19**) with 1,3-dioxane[4] (**20**) indicates a downfield shifting effect of 26.5 ppm of one ring oxygen on the other. Similarly, comparison of **21** and **24** with **22** and **25** indicates a downfield shifting

Table 2. ^{13}C shifts of cyclohexane derivatives[a]



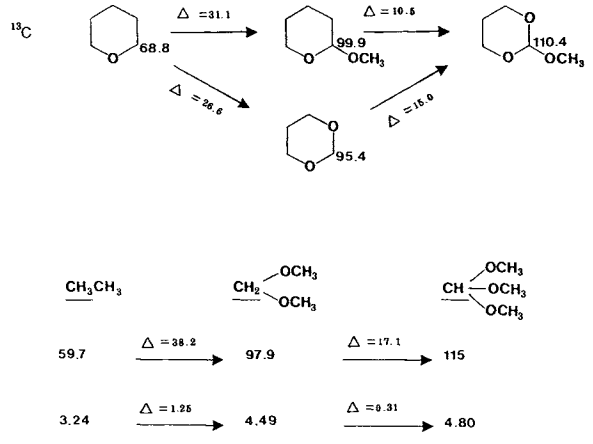
Compound	R	R'	C-1	C-2,6	C-3,5	C-4	$C(CH_3)_3$	$C(CH_3)_3$	Carbons in R	Carbons in R'
8	Me	OMe	74.6_9	36.9_2	24.5_3	48.0_4	32.2_6	27.2_6	20.2_6	48.3_6
9	OMe	Me	72.6_7	36.3_5	22.4_4	47.7_9	32.4_2	27.6_5	48.3_9	24.9_5
16	C≡CH	OH	69.4_5	40.3_4	24.8_1	47.2_2	32.4_3	27.5_3	$\beta, 72.7_3$[b] $\alpha, 87.2_7$[c]	
17	OH	C≡CH	65.7_2	39.3_7	21.8_3	47.3_0	32.2_4	27.6_5		$\beta, 70.0_2$[b] $\alpha, 89.5_5$[c]
18	OMe	OMe	99.8_6	32.8_8	23.7_2	47.7_6	32.3_0	27.6_9	47.5_1	47.4_7
39[e]	H	SOMe	60.8_0	26.3_6 25.2_8	26.5_6 26.3_6	47.3_2	32.3_9	27.4_6		35.2_7
40[e]	SOMe	H	61.4_9	27.1_7 25.0_8	22.4_1 23.1_4	47.6_9	32.5_7	27.3_6	37.1_0	
41[e]	H	SO_2Me	62.4_7	26.0_8	25.8_1	46.9_3	32.3_6	27.4_3		37.3_9
42[e]	SO_2Me	H	57.7_6	25.1_2	22.1_4	47.0_6	32.5_6	27.4_4	39.6_8 73.5_8[b]	
58	CMe_2OH	H	43.6_5	(24.1_7)[d]	(23.3_8)[d]	43.2_4	32.9_1	27.7_2	27.8_0	72.7_8[b]
59	H	CMe_2OH	49.2_1	(27.8_9)[d]	(27.4_5)[d]	48.1_4	32.2_6	27.6_0		26.9_8[c]
60	COOMe	H	39.0_0	28.0_8	23.9_1	48.0_8	32.5_2	27.4_8	51.2_9[b] 175.5_7[c]	
61	H	COOMe	43.4_8	29.6_0	26.6_4	47.4_7	32.4_1	27.5_0		51.3_3[b] 176.5_3[c]

[a] In $CDCl_3$ from internal TMS.
[b] C-β substituent (≡CH).
[c] C-α substituent.
[d] These assignments may have to be reversed.
[e] Data taken from Ref. 8.

effect of 26–31 ppm of an exocyclic axial oxygen (in this case replacing a hydrogen rather than a CH_2 group) on the endocyclic oxygen; the effect of an equatorial exocyclic oxygen (cf. **23** vs **21**, **26** vs **24**) is appreciably larger, 40–41 ppm (these are combined β- and γ-effects). Comparison of **22** or **25** with **4**, and of **23** or **26** with **3**, indicates effects of the ring oxygen on axial and equatorial exocyclic methoxy groups of 30–32 and 26–27 ppm, respectively. An effect of similar magnitude (26.5 ppm) is seen[12] in the progression from Me_2CHOMe to $Me_2C(OMe)_2$. In contrast, introduction of a third oxygen has a much smaller effect—compare **22** and **25** with **27**, or **23** and **26** with **28**; the effect of the second ring oxygen on the exocyclic oxygen is only 2–7 ppm. The same is true for the ring oxygen shift: comparison of **27** with **22** and **25** shows a downfield shifting effect of one ring oxygen on the other of only 5.5 and 12.9 ppm, respectively; corresponding data for **28** vs **23** and **26** indicate downfield shifts of 8 and 12.3 ppm. Similarly, small shifts are seen in the comparison of **27** and **28** with **29** on introduction of the exocyclic methoxy group: the axial MeO causes downfield shifts of 11–12 ppm, the equatorial MeO 24–25 ppm. These effects are much smaller than those of the second oxygen in the oxane series (see above). This suggests saturation with respect to β-O effects (replacement of CH_2 or H by O) in the ^{17}O spectra of acetals; it is, of course, well known that similar saturation occurs with respect to α-effects in the ^{13}C spectra of acetals[13] and with respect to β-effects in the proton spectra of the same class of compounds (cf. Scheme 3).[14]

Compound **30** (relative to **27**) shows a 5.7 ppm downfield shift of the exocyclic oxygen due to the β-Me group. The corresponding shift in the cyclohexane analog (**9** vs **4**, Scheme 1) is 10.7 ppm. Here, also, there seems to be some (slight) saturation effect.

The shift of the exocyclic oxygen in the unbiased system **31** is closer to that in the axial model **27** than to that in the equatorial model **28**, since the anomeric effect causes axial alkoxide to predominate in the conformational equilibrium of **31**. The anomeric



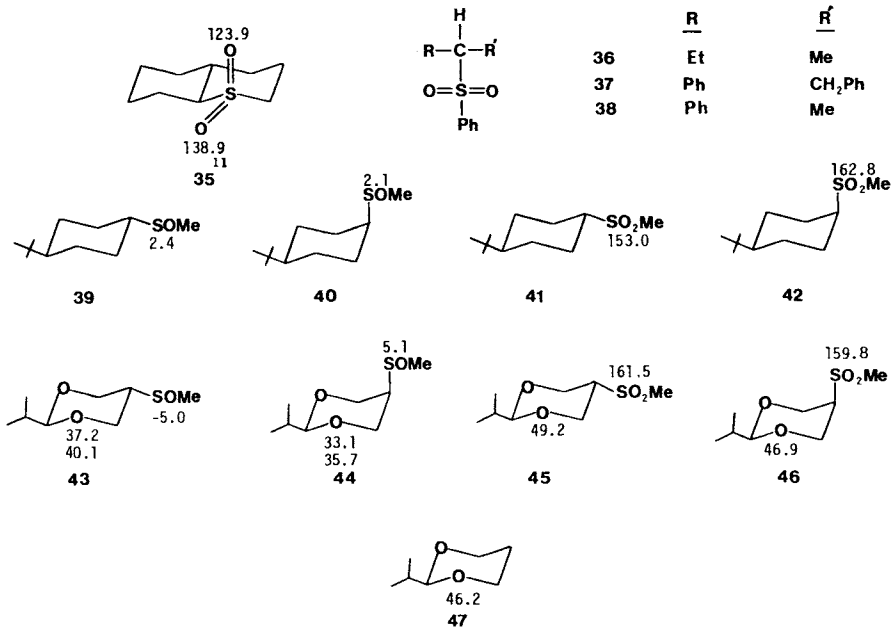
Scheme 3

equilibrium is about 2:1 in favor of the axial conformer,[15] in accord with the chemical shift in **31**.

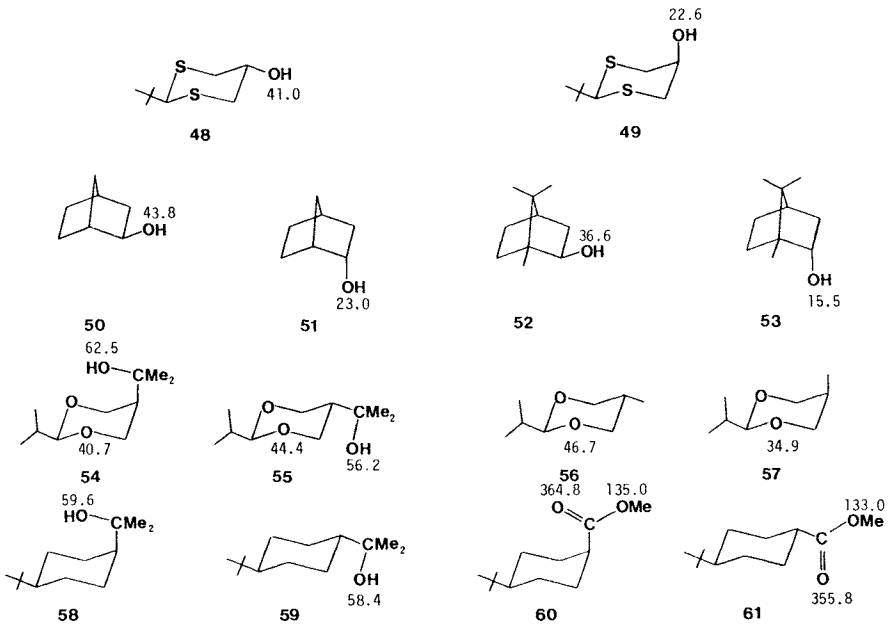
The trimethyldioxane derivatives **33** and **34** were synthesized for comparison with their previously studied cyclohexyl analogs.[1] As in the cyclohexyl series, the three methyl groups have little effect on the equatorial methoxy shift (compare **34** with **28**). However, the axial methoxy in **33** suffers a δ-compression shift of 10.5 ppm (downfield) relative to the model **27**. Unfortunately, in the cyclohexyl series only the alcohols are available for comparison; there the downfield shift is 6.9 ppm. The differences between the dioxane and cyclohexane series are not large and may, in part, reflect comparison of alcohols with ethers; on the other hand, a larger effect in the dioxane series would be reasonable on the grounds that the compression is greater because of the shorter bonds in the intervening C—O—C (as compared with C—C—C) sequence of ring atoms. The downfield shifting effect of the methoxy groups on the ring oxygen shifts in **33** and **34** relative to **32** is attenuated by saturation, in a manner similar to the series **26–28**.

We now turn to the sulfones and sulfoxides shown in Scheme 4. Dyer *et al.*[16] had already observed anisochrony of the diastereotopic oxygen nuclei in **35** and Kobayashi *et al.*[17] had observed two signals in ^{17}O-enriched 1-phenylethyl and 1-phenylpropyl sulfones. Because of improved spectral resolution, we have now been able to see distinct ^{17}O signals at natural abundance in **37** (140.3 and 145.4 ppm) and **38** (140.1 and 143.3 ppm); however, in **36**, where the difference in environment of the diastereotopic ^{17}O nuclei is merely due to the difference between methyl and ethyl at the adjacent chiral center, only a single resonance was seen at 141 ppm.

The equatorial and axially substituted cyclohexyl methyl sulfoxides **39** and **40**, respectively, display nearly the same ^{17}O chemical shift. Evidence has previously been adduced[8] that the axial sulfoxide is primarily in the conformation with the lone pair pointing towards the inside of the ring and the oxygen (and methyl) towards the outside. Therefore, the two oxygen atoms (equatorial and axial S—O) should find themselves in similar environments, in accord with their similar shifts. In the sulfones **41** and **42** it is otherwise: in the axial isomer (**42**) one of the substituents on the tetracoordinate sulfur atom must point into the ring—probably one of the (smaller) oxygen atoms rather than the (larger) methyl group. The oxygen in **42** is therefore subject to a δ-compression effect by C-3, 5, leading to a downfield shift. In contrast, this is not true for the dioxanyl sulfones **45** and **46**, whose oxygen resonances are nearly identical. It has been shown elsewhere, largely on the basis of long-range proton coupling between the methyl group and H-5,[18] that the sulfone group in **46** exists largely with the methyl group inside the ring (presumably due to O–O repulsion). Therefore, there is little or no δ-compression shift in this case. The ^{17}O shifts of the sulfoxides **43** and **44** are less simple to interpret. The difference of 7.4 ppm between the equatorial isomers **43** and **39** is most likely a through-bond effect (inductive or electrostatic) of the ring oxygens, although a difference in rotamer population about the C—S bond resulting from dipole–dipole interactions in **43** is not entirely excluded. The difference between **40** and **44** is in the opposite direction. An O-inside conformation leading to a compression effect in **44** seems highly unlikely. There is, however, an attractive through-space interaction between the ring oxygens and the sulfur which stabilizes **44** over **43** (and **46** over **45**);[18] this interaction may cause the small downfield shift in **44** relative to **40**. The ring oxygen nuclei in **43** and **44** are anisochronous, as expected on the basis of their diastereotopicity (owing to chirality of the sulfoxide moiety); similar anisochrony is seen in the ^{13}C signals of C-3 and C-5 in **39** and **40**.[8] The effect of the sulfoxide function on the ring oxygens is upfield shifting (relative to **47**), whereas the effect of the sulfone function (in **45** and **46**) is downfield shifting. In both



Scheme 4



Scheme 5

series the ring oxygen nuclei of the axial isomers (**44**, **46**) resonate upfield of those of their equatorial isomers (**43**, **45**), presumably because of the usual γ-upfield shift caused by an axial substituent.[4]

In Scheme 5 are shown some miscellaneous compounds examined. Compounds **48** and **49** display ^{17}O shifts similar to those of the carbocyclic analogs **1** and **2**, and different from the corresponding dioxanyl alcohols.[1] In particular, the large upfield-shifting γ-*anti* effect seen in the equatorial dioxanol is not seen in the dithiane analog. This is in accord with similar observations regarding γ-*anti* effects of ^{13}C nuclei.[3] The norbornane and bornane derivatives **50–53** are unexceptional; the *endo*-OH is upfield of the *exo*-OH, and an additional upfield shift results from angular methyl in the bornane derivatives (γ-effects). The tertiary alcohol **54** exists predominantly with the OH-inside conformation;[19] accordingly, its OH ^{17}O resonance is downfield of that of the stereoisomer **55** (δ-compression effect).* Demonstration of a reciprocal compression effect on the ring oxygen signals is more difficult, since the ring-O signals in **54** are upfield of those in **55**. However, it must be considered that the axial substituent at C-5 also produces a γ-*gauche* (upfield) effect which, in this case, outweighs the downfield δ-effect. Comparison with the models **56** and **57** suggests that there *is* a δ-effect superimposed on the γ-effect in **54**, for whereas the ring oxygens in **55** are within 2.3 ppm of those of **56**, the difference between **54** and **57** (5.8 ppm) is appreciably larger. Demonstration of a δ-effect in the carbocyclic analog **58** by comparison with **59** failed; ^{13}C spectra (Table 2) suggest that **58** is not conformationally homogeneous, having contributions from alternate chair and/or twist forms.

Esters **60** and **61** were intermediates in the synthesis of **58** and **59**. Surprisingly, both the acyl and (to a lesser extent) the alkyl oxygen in the equatorial isomer **62** are upfield of their axial counterparts in **61**.

Some of the ^{17}O chemical shifts observed here find ready explanation in substituent, compression and saturation effects similar to those seen in the ^{13}C NMR spectra. There are, however, some shifts, notably in the sufoxides, which cannot be explained entirely in this way.

^{13}C NMR spectra

In Tables 2 and 3, ^{13}C NMR spectra of selected compounds described here are reported. The following observations from these tables are worth mentioning. (a) The carbinolic carbon in **55** shows an upfield shift (compared with **58**) arising from γ-antiperiplanar oxygens.[3] (b) The substituent effects are $\alpha_{axial} > \alpha_{equatorial}$ for —SOMe and —SO_2Me groups in all compounds studied. (c) The sulfoxides (**39**, **40**, **43**, and **44**) show different signals for diastereotopic carbons.[8]

EXPERIMENTAL

The ^{17}O spectra were recorded on a Bruker spectrospin WM-250 spectrometer equipped with a 10-mm probe at 33.91 MHz in the FT mode without a lock.

* A referee has suggested that the downfield shift of the hydroxyl oxygen in **54** might be due to intramolecular hydrogen bonding, since it is known that intermolecular hydrogen bonding leads to sizeable downfield shifts (*ca* 12 ppm) in the oxygen atom of the donor group (with a smaller shift of about 6 ppm in the acceptor oxygen).[20] We consider this interpretation unlikely for the following reasons. (1) Intramolecular hydrogen bonding in compound **54** is known, from IR studies, to be weak.[19] (2) Although intramolecular hydrogen bonding in *cis*-5-hydroxy-2-isopropyl-1,3-dioxane (similar to **54** but with axial OH in lieu of CMe_2OH) is known to be strong, hydrogen bonding was rejected as the major explanation of its observed downfield ^{17}OH shift (relative to its equatorial or *trans* counterpart) in the previous paper,[1] since a nearly equal downfield shift is observed in the corresponding axial methyl ether relative to the equatorial compound.[1]

Table 3. ^{13}C shifts of 1,3-dioxanes[a]

Compound	C-2	C-4	C-5	C-6	OMe	2-Me	4-Me	6-Me	$(\underline{C}H_3)_2CH$	$(CH_3)_2\underline{C}H$	$\underline{C}Me_2$	$C\underline{Me}_2$
27[d]	109.0_4	64.7_0	32.0_1	58.4_3	52.6_4		21.2_9					
28[d]	112.0_3	71.6_8	32.5_7	64.0_1	52.5_0		21.5_3					
30	112.1_9	64.7_7	31.9_0	59.3_8	50.3_0	22.7_3	21.6_3					
31	110.4_0	61.8_1	24.9_0	61.8_1	52.5_6							
32	87.7_9	71.1_5	44.3_0	68.6_2			31.6_3 (e) 21.5_9 (a)	21.7_9				
33[d]	109.8_8	71.4_7	43.4_9	60.7_0	52.7_0		31.8_7 (e) 27.4_8 (a)	21.4_2				
34[d]	107.9_2	73.3_1	42.6_3	67.2_9	51.8_5		31.3_8 (e) 23.1_4 (a)	21.3_4				
43	105.8_1	(65.4_5)	53.0_6	(64.2_8)	36.2_6[b]				16.8_7	32.4_9		
44	106.1_1	(63.5_5)	56.4_5	(62.4_6)	37.2_3[b]				16.6_7	32.7_1		
45[c]	105.8_5	64.9_8	56.2_3	64.9_8	40.1_7[b]				16.8_4	32.7_2		
46[c]	106.4_4	65.2_7	59.4_1	65.2_7	43.0_4[b]				16.8_4	33.0_3		
54	105.8_3	67.2_5	42.9_7	67.2_5					16.7_2	32.7_2	72.3_1	29.4_4
55	105.7_0	68.2_6	44.5_4	68.2_6					17.1_4	32.6_2	69.9_0	27.6_0

[a] In $CDCl_3$ from TMS unless specified otherwise.
[b] Methyl of the sulfinyl group.
[c] Solvent: acetone-d_6–$CDCl_3$ (50:50, v/v).
[d] Peak assignment from mixture of epimers.

Samples (natural ^{17}O abundance) were 1 M solutions in toluene (dried over anhydrous $CaCl_2$) in 10-mm tubes, heated to 100 °C. The spectral settings were as follows: 4–20 kHz spectral width, 128–1000 data points, 90° pulse angle corresponding to a 30 μs pulse width, 5–30 ms acquisition time with a 250 μs acquisition delay and 10^4–10^6 scans. Under these conditions, the observed signals had half band-widths in the range 100–200 Hz. Chemical shifts were measured without proton decoupling and are reported relative to external tap water as reference at 100 °C. Although they were read to 0.1 ppm, their reproducibility is probably no better than 2–3 ppm.

For some of the compounds the data collection was done by a quadrupole echo experiment, the pulse program for which was kindly given to us by Professor P. D. Ellis. Carbon-13 NMR spectra were recorded on a Varian XL-100 (25.12 MHz) instrument operating in the pulsed Fourier transform mode, locked on solvent deuterium with broad-band proton decoupling. ^{13}C NMR samples were prepared as 10–15% solutions in $CDCl_3$.

Materials

Compounds **6**, **7**, **10**,[6] **11**,[6] **14** and **15** were obtained in the course of the doctoral research of E. Juaristi[21] by the addition of the appropriate Grignard reagent to 4-*tert*-butylcyclohexanone, and the chromatographic separation of the resulting diastereomers. Alcohols **12** and **13** have been described elsewhere[6] and **16** and **17** were synthesized according to a reported procedure.[22]

Ethers **8** and **9** were synthesized from the corresponding alcohols **6** and **7** employing the CH_3I–NaH–THF procedure.[23]

8: b.p. 100–105 °C/18 mmHg (Kugelrohr). ^{13}C NMR: Table 2. MS: 184, 169, 85. Elemental composition: calculated for $C_{12}H_{24}O$, M^+ 184.183; found, 184.183.

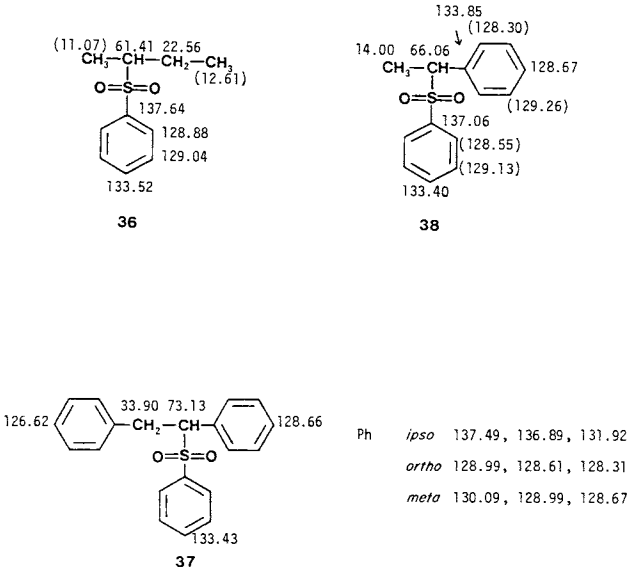
9: b.p. 98–100 °C/20 mmHg (Kugelrohr). ^{13}C NMR: Table 2. MS: 184, 169, 85. Elemental composition: calculated for $C_{12}H_{24}O$, M^+ 184.183; found, 184.183.

Compound **18** was synthesized according to the procedure described in Ref. 24.

Acyclic sulfones. ^{13}C NMR spectra of sulfones **36–38** are reported in Scheme 6. Sulfone **37** was obtained by adding thiophenol to stilbene in the presence of $HClO_4$[25] and oxidizing the resulting sulfide with excess of H_2O_2–HOAc. M.p. 147 °C (lit.,[26] 147 °C). Sulfone **38** was similarly prepared from styrene. M.p. 117–120 °C (lit.,[27] 119–120 °C).

To obtain **36**, *sec*-butyl bromide was heated for 24 h at 115 °C with sodium thiophenolate, and the resulting sulfide was oxidized with H_2O_2–HOAc to *sec*-butyl phenyl sulfone. B.p. 123 °C/2 mmHg (lit.,[28] 113–115 °C/0.2 mmHg).

Dioxanes. Compound **32** was synthesized as reported.[29] Compounds **27**, **28**, **30**, **31**, **33** and **34** have



Scheme 6

been reported by Eliel and Nader.[15] Tertiary carbinols **54** and **55** were obtained from the corresponding acids (esterification using CH_2N_2 followed by CH_3MgI addition) according to the method of Eliel and Banks.[19]

Carbon-13 NMR spectra. ^{13}C NMR spectra not previously reported for compounds described here are recorded in Tables 2 (for cyclohexanes) and 3 (for 1,3-dioxanes).

Other compounds. Cyclohexyl sulfoxides and sulfones[8] **39–42** and dioxanyl sulfoxides and sulfones[18] **43–46** have been reported earlier.

4-*tert*-Butylcyclohexane-1-carboxylic acid (50:50 *cis–trans* mixture) (ICN Pharmaceuticals) was esterified with CH_2N_2. The mixture of esters was separated by gas–liquid chromatography using a Carbowax 20M column at 155 °C, **60** being eluted first followed by **61**. Grignard addition of CH_3MgI to **60** yielded **58**, and similar treatment of **61** yielded **59**.[30] ^{13}C NMR: Table 2.

The data for other compounds, used as model compounds in the text, have been taken from the references[1,4,5] mentioned therein.

Acknowledgements

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