Carbon-13 Nuclear Magnetic Resonance Spectra of 9-Thiabicyclo[3.3.1]nonanes

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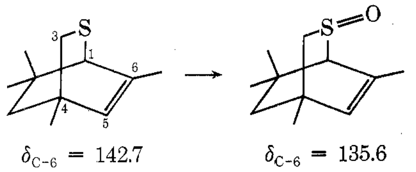
The carbon-13 NMR spectra of a number of sulfides and sulfones in the 9-thiabicyclo[3.3.1]nonane geometry are reported and discussed. Upon conversion of a sulfide to a sulfone, the carbons γ to the oxygen experience upfield shifts; other substituent effects also are described. Incorporation of a 2,3 double bond into the bicyclic nucleus induces an upfield shift of carbon 7 as a consequence of the relief of δ transannular steric interactions. The effects of the configuration of a 2-hydroxyl group on chemical shifts are reported.

Carbon-13 nuclear magnetic resonance spectroscopy has evolved into a very powerful technique for structure elucidation in organic chemistry.[1-3] One of the most useful features of ^{13}C NMR is that steric interactions generate significant shielding or deshielding contributions to the resonance frequency of congested carbon atoms. Because of this sensitive dependence of the carbon chemical shift upon molecular geometry, ^{13}C NMR is especially valuable in conformational analysis.[4] Upon the replacement of a hydrogen atom with a functional group (including alkyl and aryl groups), the carbon bearing the functionality (the α carbon) and the carbon immediately adjacent to the carbon containing the substituent (the β carbon) usually experience downfield shifts. On the other hand, the carbons γ to the substituent usually exhibit upfield shifts. Grant and Cheney[5] have proposed that "the upfield shifts are due to (sterically) induced polarization of charge along the HC^{13} bond" when the γ carbon is in a gauche relationship with the substituent.[6-12] For γ-eclipsed nuclei (such as in cis-disubstituted olefins[13] and ortho-disubstituted aromatics[14]), upfield shifts are also found,[15] presumably for similar steric reasons. While the upfield γ steric argument has been very valuable in assignment of chemical shifts as well as a convenient indicator of spatially proximate groups, it should be employed with care since a substantial amount of data has been presented for δ steric effects which are uniformly downfield.[16-18] Moreover, Eliel et al. recently have demonstrated that appreciable upfield shifts are observed even when the γ carbon and the substituent are in an antiperiplanar arrangement (thus precluding steric effects), but only when the substituent is a second row heteroatom (N, O, F).[19]

We have measured the ^{13}C NMR spectra of 9-thiabicyclo[3.3.1]nonane (1) and a number of its derivatives. In this report we describe the effects on the carbon chemical shifts of these bridged bicyclic substrates as a function of (1) the conversion of a sulfide to a sulfone, (2) the incorporation of a 2,3 double bond into the bicyclo[3.3.1]nonyl geometry, and (3) the configuration of a 2-hydroxyl group.

Results and Discussion

Effect of the Oxidation of Sulfur. For the transformation shown in eq 1, the introduction of an oxygen on sulfur results in the γ-gauche carbon 6 being shielded by 7.1 ppm.[20] Similar γ-gauche steric effects have been reported for trimethylene sulfites,[21] 1,4-oxathiane,[22] and the parent thiane system.[23]



(1)

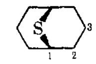
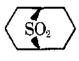
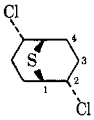
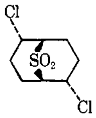
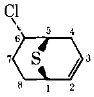
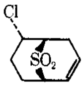
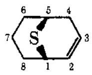
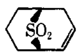
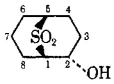
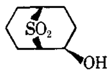
$\delta_{C\text{-}6} = 142.7$ $\delta_{C\text{-}6} = 135.6$

The ^{13}C chemical shifts for the 9-thiabicyclo[3.3.1]nonanes we have studied are listed in Table I. Assignments were made in the following manner. The shieldings of the parent sulfide 1 and sulfone 2 were apparent from relative peak intensities and the splitting patterns observed in coupled spectra; the assignments are unambiguous. For the 2,6-dichlorides (3 and 4) the known[24] effects of an endo 2-chloride in the bicyclo[3.3.1]nonane system were employed in conjunction with coupled spectra to assign the signals to the proper carbons.[25] With our data for compounds 1–4, along with other information for various bicyclo[3.2.1]oct-2-enes,[26] chemical shift assignments for the carbons of the unsaturated sulfides and sulfones 5–8 followed in a straightforward way. In accord with the results of Stothers et al.,[26] the lower field olefinic resonance is assigned to olefinic carbon 2, adjacent to the bridgehead. In all cases, coupled spectra were obtained in order to distinguish positively between the methylene and methine carbon atoms.

From the data assembled in Table I, the substituent parameters of transforming a sulfide to a sulfone in the 9-thiabicyclo[3.3.1]nonane system can be derived; they are summarized in Table II. The effect on the bridgehead carbons (β effect) is 20.0 ppm, a value virtually identical with that reported for the 2-thiabicyclo[2.2.2]octane system.[24] The deshielding direction of the β effect reflects the greater electron-withdrawing inductive nature of the sulfonyl moiety compared to the sulfide group. The γ effects are shielding (presumably owing to gauche steric interactions) and are dependent upon the proximity of any chlorine atoms in the molecule. For the aliphatic γ carbon atoms *without an α or γ chlorine* (γ aliphatic effect *type I*) the sulfonyl oxygen produces upfield shifts of about −2.4 ppm; this effect is in close agreement with that found for the conversion of 1,4-oxathiane to 1,4-oxathiane 4,4-dioxide.[22] γ carbons *with a γ chlorine* (γ aliphatic effect *type II*) experience upfield shifts of about −6.6 ppm upon oxidation to the dioxide. Aliphatic carbons *with an α chlorine* (γ aliphatic effect *type III*) are shielded by approximately −5.1 ppm as a result of the sulfide to sulfone transformation. The olefinic γ carbons are shifted to higher field by 8.5 ppm; a similar shielding has been observed for the 2-thiabicyclo[2.2.2]octene system.[20] At the present time we are unable to offer a satisfactory explanation for the effect of chlorine on the γ aliphatic effects of types II and III. The δ aliphatic effect is −2.5 ppm; similar δ oxidation effects have been reported for the production of thiane 1-oxide[23] from thiane,[19] as well as for the conversions of hydrocarbons to ketones in the bicyclo[3.3.1]nonyl,[24,27] bicyclo[3.2.1]octyl,[26] and adamantyl[11,28] systems. The δ olefinic effect (1.6 ppm) is in substantial agreement with previous results.[20]

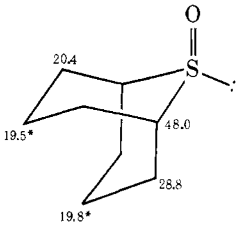
In order to gain some insight of the effect of monooxida-

Table I. ^{13}C Chemical Shifts for Various 9-Thiabicyclo[3.3.1]nonanes[a]

Carbon	 1	 2	 3	 4	 5	 6	 7	 8	 16	 17
1	33.2	53.2	37.3	56.7	31.4	52.5	33.6	54.2	58.6	58.6
2	32.1	29.4	62.4	58.0	129.9	121.3	130.3	121.8	69.2	72.3
3	21.6	19.2	32.5	30.3	127.5	129.9	129.0	129.8	28.2	28.6
4	32.1	29.4	28.3	22.0	34.2	27.1	35.3	32.6	25.2	25.9
5	33.2	53.2	37.3	56.7	38.9	58.4	32.8	52.5	51.9	52.7
6	32.1	29.4	62.4	58.0	64.4	57.9	30.6	28.2	29.2	28.6
7	21.6	19.2	32.5	30.3	25.7	26.0	18.0	14.7	18.6	17.4
8	32.1	29.4	28.3	22.0	28.8	27.1	32.8	31.1	28.2	26.8

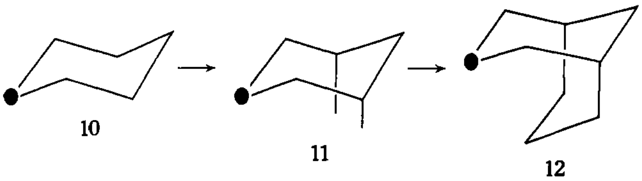
[a] In parts per million from internal Me_4Si for $CDCl_3$ solutions.

tion, the bicyclic sulfoxide 9 was also studied; its chemical shifts are shown with its structure. The coupled spectrum



permits an unequivocal assignment for the bridgehead carbons. The other assignments were based upon the data for thiane 1-oxide[23] and 1,4-oxathiane 4-oxide.[22] For the carbons of the ring in which the oxygen is axial, and γ and δ effects are −11.7 and −2.1 ppm; these values are very similar to those found for thiane 1-oxide (−12.3 and −1.8 ppm, respectively).[19,23] For the carbons of the ring in which the oxygen is equatorial, the γ and δ effects are −3.3 and −1.8 ppm; the corresponding values for the monocyclic model are −4.5 and −1.8 ppm, respectively.[19,23] The γ-gauche effect is a result of steric interactions similar to those exhibited in the sulfide to sulfone transformations described above, although the magnitude is substantially greater for the sulfoxide.[22] The γ-anti effect is not unlike those reported by Eliel[19] and may have the same origin. The β effect (14.8 ppm) is substantially less than those in the parent thiane system (15.9 ppm for axial oxygen and 23.0 ppm for equatorial oxygen).

Effect of Incorporating a 2,3 Double Bond into the 9-Thiabicyclo[3.3.1]nonane System. Introduction of two axial methylene groups onto a six-membered ring in a 1,3 fashion (10 → 11) should bring about an upfield shift of the



10 11 12

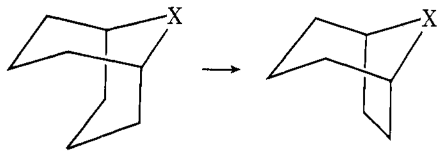
unsubstituted γ carbon by approximately 10 ppm[6-12] as a consequence of the γ-gauche steric effect. Tying the methylene groups together with another methylene unit provides the bicyclo[3.3.1]nonane geometry (11 → 12) and adds a deshielding increment to the chemical shift of the carbon atom under consideration as a result of the δ steric effect. From the data collected in Table III, the overall effect on the chemical shift of the designated carbon for the conversion of a (hetero)cyclohexyl substrate into a (9-hetero)bicyclo[3.3.1]nonyl derivative is approximately −5.3 ppm, which implicates a δ steric shift of about 4.7 ppm (a value in good agreement with other reported δ shifts[16-18]).

Table II. Substituent Parameters for Sulfide to Sulfone Conversion

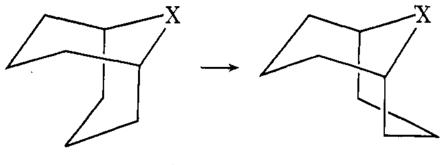
Parameter[a]	Occurrences[b]	$\Delta\delta$, ppm	Range	Standard deviation
β	c	+20.0	19.4 to 21.1	0.7
γ aliphatic I	d	−2.4	−1.7 to −2.7	0.5
γ aliphatic II	e	−6.7	−6.3 to −7.1	0.6
γ aliphatic III	f	−5.4	−4.4 to −6.5	1.5
γ olefinic	g	−8.6	−8.5 to −8.6	0.1
δ aliphatic	h	−2.6	−2.2 to −3.3	0.6
δ olefinic	i	+1.6	0.8 to 2.4	1.1

[a] See text for explanation of types. [b] The number of independent measurements, N, is used to calculate the mean and standard deviation for each effect. [c] 1 → 2, C-1, 5; 3 → 4, C-1, 5; 5 → 6, C-1, 5; 7 → 8, C-1, 5; $N = 6$. [d] 1 → 2, C-2, 4, 6, 8; 7 → 8, C-4, 6, 8; $N = 4$. [e] 3 → 4, C-4, 8; 5 → 6, C-4; $N = 2$. Not included is value of −1.7 for 5 → 6, C-8. [f] 3 → 4, C-2, 6; 5 → 6, C-6; $N = 2$. [g] 5 → 6, C-2; 7 → 8, C-2; $N = 2$. [h] 1 → 2, C-3, 7; 3 → 4, C-3, 7; 7 → 8, C-7; $N = 3$. Not included is value of +0.3 for 5 → 6, C-7. [i] 5 → 6, C-3; 7 → 8, C-3; $N = 2$.

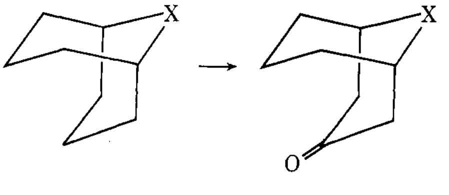
Elimination of the transannular interaction inherent in the chair–chair conformation of the bicyclo[3.3.1]nonane nucleus should remove the δ steric component of the encumbered carbons and induce an upfield shift. There are at least four ways of eliminating or reducing the transannular (δ) steric interaction in bicyclo[3.3.1]nonanes: (1) conversion of the [3.3.1]nucleus to the [3.2.1]nucleus[18a,26,27,30] (eq 2); (2) alteration of the chair–chair to chair–boat equilibrium in favor of the latter[18,31] (eq 3); (3) transformation of a 3-methylene group to a 3-keto group[18,27] (eq 4); and (4) incorporation of a 2,3 double bond into the bicyclic nucleus (eq 5). Table IV contains examples pertinent to the first three types of modifications (eq 2–4). As can be seen, each



(2)

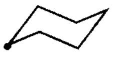
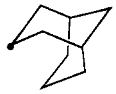
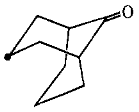
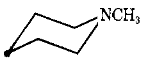
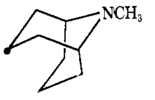
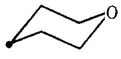
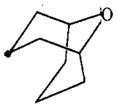
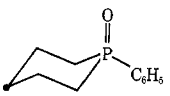
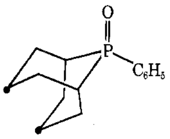
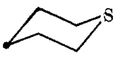
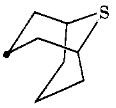
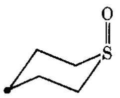
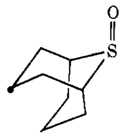
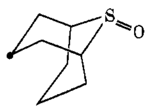


(3)



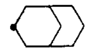
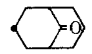
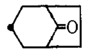
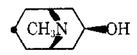
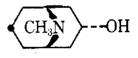
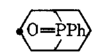
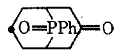
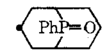
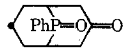
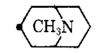
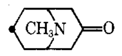
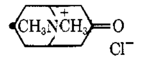
(4)

Table III. Effect on the Chemical Shift of Designated Carbons for the Conversion of (Hetero)cyclohexanes to (9-Hetero)bicyclo[3.3.1]nonanes^a

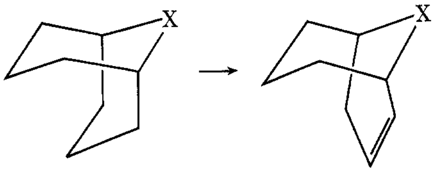
Cyclohexyl compd	Chemical shift^b	Bicyclononyl compd	Chemical shift^b	Δδ
	27.7^c		22.8^d	−4.9
	24.1^c		20.7^d	−3.4
	26.6^c		20.4^e	−6.2
	25.1^c		18.8^d	−6.3
	27.0^f		21.6^g 20.9^g	−5.4 −6.1
	26.5^h		21.6^d	−4.9
	24.7^i		19.5^j	−5.2
	24.7^i		19.8^j	−4.9

^{a} Chemical shifts of carbons denoted by •. ^{b} In parts per million from Me_4Si. ^{c} Reference 1. ^{d} Reference 27. ^{e} Reference 18a. ^{f} Reference 29. ^{g} Reference 18b. ^{h} Reference 19. ^{i} Reference 23. ^{j} This work.

Table IV. Modification of Bicyclo[3.3.1]nonanes to Relieve Transannular Interactions^a

Entry	Bicyclo-[3.3.1]-nonane	Chemical shift^b	Modified compd	Chemical shift^b	Δδ
1		22.8^c		19.1^d	−3.7
2		20.7^c		17.4^d	−3.3
3		20.4^e		15.9^f	−4.5
4		19.8^e		14.5^e	−5.3
5		18.2^e		13.0^e	−5.2
6		21.6^f		18.2^f	−3.4
7		20.9^f		17.1^f	−3.8
8		20.4^e		16.1^e	−4.3
9		18.4^e		14.8^c	−3.6

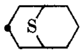
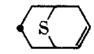
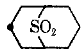
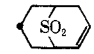
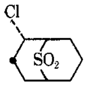
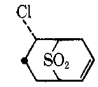
^{a,b} See Table III. ^{c} Reference 27. ^{d} Reference 26. ^{e} Reference 18a. ^{f} Reference 18b.



(5)

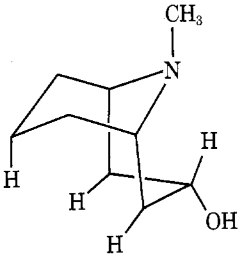
transformation produces an upfield shift of the sterically relieved carbon. Until now, there have been no examples of the type of transformation indicated in eq 5; our data are summarized in Table V and are in accord with our prediction.

Table V. Effect of Incorporation of a 2,3 Double Bond into the 9-Thiabicyclo[3.3.1]nonane Nucleus^a

Saturated compd	Chemical shift^b	Unsaturated compd	Chemical shift^b	Δδ
	21.6		18.2	−3.4
	19.2		14.7	−4.5
	30.8^c		26.0	−4.8

^{a,b} See Table III. ^{c} Reference 27.

It is of interest to point out the significance of the larger Δδ values found for the 3-hydroxy-9-methyl-9-azabicyclo[3.3.1]nonane system (Table IV, entries 4 and 5) compared to those found for all other examples of transannular steric relief (−5.3 ppm vs. about −3.9 ppm, respectively). The additional 1.4 ppm upfield shift found for the granatanol derivatives can be attributed to the γ-gauche steric interaction between the endo hydrogen on carbon 7 and the endo hydrogens at carbons 2 and 4 (see structure **13**).[18]



13

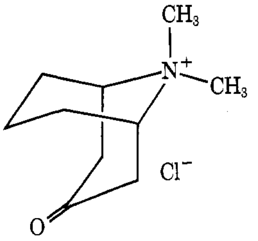
Of additional significance is the resonance position of the carbonyl carbon of pseudopelletierine methochloride (Table IV, entry 9). Jones and Hassan have demonstrated that the chemical shift of the carbonyl carbon of the methiodide of *N*-methyl-4-piperidone is solvent dependent: in dimethyl sulfoxide carbon 4 resonates at 201.7 ppm, a value typical for carbonyl carbons;[1] on the other hand, in water carbon 4 absorbs at 101.7 ppm, indicating that the carbonyl group exists as the hydrate.[31] For the pseudopelletierine derivative **14** the carbonyl carbon resonates at 193.7 ppm in water;[27] thus hydrate formation is insignificant because of steric interactions of the endo hydroxyl group in conformation **15a** or the exo hydroxyl group in conformation **15b**.

Effect of the Configuration of a 2-Hydroxyl Group. We have previously described the effects of the configuration of a 3-hydroxyl substituent in the 9-azabicyclo[3.3.1]nonane and 9-phosphabicyclo[3.3.1]nonane systems on the chemical shifts of the various carbon atoms.[18] Also of interest are the effects of the configuration of a 2-hydroxyl group. Thus, we measured the ^{13}C NMR spectra of the hydroxyl sulfones **16** and **17**; Tables I and VI contain

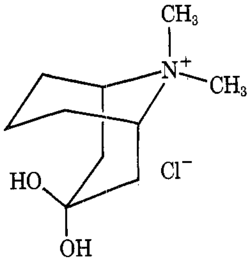
Table VI. ^{13}C Substituent Parameters for 2-Hydroxyl-9-thiabicyclo[3.3.1]nonane 9,9-Dioxides

	Δδ for carbon position^a							
Compd	1	2	3	4	5	6	7	8
16 (endo OH)	5.4	39.8	9.0	−4.2	−1.3	−0.2	−0.6	−1.2
17 (exo OH)	5.4	42.9	9.4	−3.5	−0.5	−0.8	−1.8	−2.6

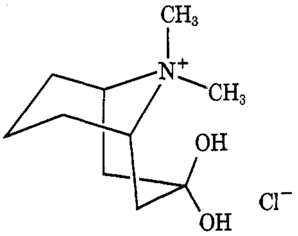
^{a} Δδ values are differences in chemical shifts (in parts per million) observed upon introduction of 2-hydroxyl group into parent sulfone **2**.



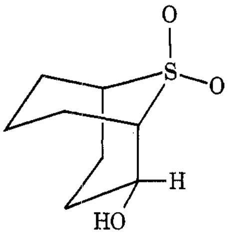
14



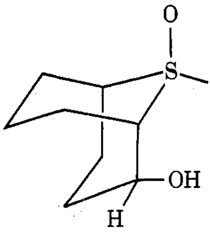
15a



15b



16



17

the pertinent chemical shift information. Assignments were made on the basis of the well-documented substituent effects of hydroxyl groups,[1,19] splitting patterns of coupled spectra, and with the aid of the other sulfone data obtained in the present investigation. Since the completion of our study, a report on the configurational effects of a 2-hydroxyl group in the bicyclo[3.3.1]nonan-2-one system has appeared;[24] our data are completely compatible with those reported, but will not be elaborated here in view of the extensive discussion in the published account.[24]

Experimental Section

^{13}C NMR spectra were measured at 25.15 MHz with a JEOL JNM PS-100 spectrometer interfaced with a Nova 1200 computer operating in the 8K mode. "Coupled spectra" were run fully coupled rather than off-resonance decoupled. All of the 9-thiabicyclo[3.3.1]nonane derivatives were run in deuteriochloroform with Me_4Si as internal standard. In all cases 10-mm tubes were employed, and the sample concentrations were on the order of 0.5 M. With the exception of **17**,[32] all of the 9-thia substrates were prepared and purified according to literature procedures: **1**,[33] **2**,[33] **3**,[33] **4**,[33] **6**,[34] **7**,[34] **8**,[34] **9**,[33] and **16**.[34]

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Registry No.—**1**, 281-15-2; **2**, 6522-45-8; **3**, 10502-30-4; **4**, 6522-46-9; **5**, 6522-22-1; **6**, 58703-11-0; **7**, 13334-79-7; **8**, 6435-90-1; **16**, 58240-76-9; **17**, 58240-77-0.

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