chemical shift of each signal, relative to the reference methyl iodide signal. All the chemical shifts reported here have been corrected to a Me_4Si reference by the relationship

$$\text{ppm}\ (Me_4Si) = \frac{H_2\ (\text{obsd}) - 977 - T(°C) \times 0.70}{25.2}$$

The ^{13}C NMR spectra for the remaining heteroorganic ions and precursors were obtained on a Varian Associates Model XL-100 spectrometer equipped with a broad decoupler and variable temperature probe. The instrument operates at 25.2 MHz for carbon-13, and is interfaced with a Varian 620L computer. The combined system was operated in the pulse Fourier transform mode, employing a Varian Fourier transform accessory. Typically 3000–5000 pulses, each of width 20–30 μs, needed to be accumulated in order to give a satisfactory signal to noise ratio for all signals of interest. Field frequency stabilization was maintained by locking on the fluorine-19 external sample of fluorobenzene. Chemical shifts were measured from the carbon-13 signal of 5% carbon-13 enriched tetramethylsilane in a 1.75-mm capillary held concentrically inside the standard 12-mm sample tube.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

Registry No.—**1a**, 288-53-9; **1a**-H$^+$, 62139-47-3; **1a**-CH_3^+, 62139-48-4; **1b**, 930-35-8; **1b**-H$^+$, 62139-49-5; **1b**-CH_3^+, 56125-66-7; **2**, 2171-74-6; **2**-H$^+$. 62139-50-8; **3**, 6823-42-3; **4**, 39525-29-6; **5**, 274-31-7.

References and Notes

(1) (a) Part 8: G. A. Olah, J. S. Staral, G. Liang, L. A. Paquette, W. P. Melenga and M. J. Carmody, *J. Am. Chem. Soc.*, in press. (b) Address correspondence to the Department of Chemistry, University of Southern California, Los Angeles, Calif. 90007.
(2) J. P. Snyder, Ed., "Nonbenzenoid Aromatics", Academic Press, New York, N.Y., 1969; D. Ginsberg, Ed., "Non-Benzenoid Aromatic Compounds", Interscience, New York, N.Y., 1959; E. D. Bergmann and B. Pullman, Ed., "Aromaticity, Pseudo Aromaticity, Anti-Aromaticity", Israel Academy of Sciences and Humanities, Jerusalem 1971; G. Binsch, *Naturwissenschaften*, **60**, 369 (1973); R. Breslow, *Acc. Chem. Res.*, **6**, 393 (1973).
(3) S. McElvain and I. Venerable, *J. Am. Chem. Soc.*, **72**, 1661 (1950); K. Dimroth and K. Schromm, *Angew. Chem., Int. Ed. Engl.*, **4**, 873 (1965); G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, **90**, 1884 (1968); H. Perst, "Oxonium Ions in Organic Chemistry", Academic Press, New York, N.Y., 1971, p 8–10.
(4) W. R. H. Hurtley and S. Smiles, *J. Chem. Soc.*, 1821 (1926); 534 (1927); F. Challenger, E. A. Mason, E. C. Holdsworth, and R. Emott, *J. Chem. Soc.*, 292 (1953); L. Soder and R. Wizinger, *Helv. Chim. Acta*, **42**, 1733 (1959); J. Teste and N. Lozach, *Bull. Soc. Chim. Fr.*, 437 (1955); E. Klingsberg, *Chem. Ind. (London)*, 1568 (1960); D. Leaver and W. A. H. Robertson, *Proc. Chem. Soc., London*, 252 (1960); R. Mayer and B. Gebhardt, *Chem. Ber.*, **97**, 1298 (1964); A. Luttringhaou, H. Berger, and H. Prinzbach, *Tetrahedron Lett.*, 2121 (1965); E. Campaigne and R. D. Hamilton, *J. Org. Chem.*, **29**, 2877 (1964); R. Gompper, E. Kutter, and H. Wagner, *Angew. Chem., Int. Ed. Engl.*, **5**, 517 (1966); T. Nakai, *J. Synth. Org. Chem. Japan.*, **28**, 708 (1970).
(5) R. Zahradnik and J. Kontecky, *Tetrahedron Lett.*, 632 (1961).
(6) (a) G. A. Olah, "Carbocations and Electrophilic Reactions", Wiley, New York, N.Y., 1974, pp 102–111, and references given therein; (b) G. A. Olah, D. J. Donovan, and H. C. Lin, *J. Am. Chem. Soc.*, **98**, 2661 (1976), and references given therein.
(7) E. Klingsberg, *J. Am. Chem. Soc.*, **86**, 5290 (1964).
(8) (a) P. C. Lauterbur, *J. Chem. Phys.*, **38**, 1406 (1962); **38**, 1415, 1432 (1963). (b) P. Lazzeretti and F. Taddei, *Org. Magn. Reson.*, **3**, 283 (1971); J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972.
(9) D. M. Grant and E. M. Daub, *J. Am. Chem. Soc.*, **86**, 2984 (1964).
(10) D. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.*, **89**, 6612 (1967).
(11) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972, pp 59–78.
(12) L. Pauling, "The Chemical Bond", Cornell University Press, Ithaca, N.Y., 1967.
(13) H. Volz and G. Zimmerman, *Tetrahedron Lett.*, 3597 (1970).
(14) The ^1H NMR spectrum resulting from the treatment of **3**-SO_2 with FSO_3H–SO_2 deviates from that reported by Volz and Zimmerman.[13] Two singlets, δ 4.8 and 4.5, are observed for dimethoxycarbenium ion (see similar spectral and multiplicity assignments according to Borch[15]) and a singlet δ 4.3 corresponding to the methyl protons of methyl fluorosulfonate.[16]
(15) D. Buza, A. Gyrff-Keller, and S. Szymanski, *Rocz. Chem.*, **44**, 2319 (1970). We wish to express our appreciation to Dr. J. Bukala for his assistance in translating this article.
(16) S. Petersen in Houben-Weyl "Methoden der Organischen Chemie", Vol. 8, Georg Thieme Verlag, Stuttgart, 1952, p 109.
(17) R. Ernst, "Advances in Magnetic Resonance", Vol. 2, Academic Press, New York, N.Y., 1966, p 74 ff.
(18) A. Abragam, "Principles of Nuclear Magnetism", Oxford University Press, London, 1961, p 114.
(19) G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, **90**, 1884 (1968).

Carbon-13 Nuclear Magnetic Resonance Spectra of Bridgehead Substituted Bicyclo[3.3.1]nonanes

John R. Wiseman* and Herman O. Krabbenhoft

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

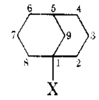
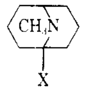
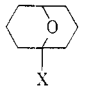
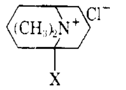
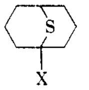
Received February 22, 1977

The ^{13}C NMR spectra of several bicyclo[3.3.1]nonanes, 9-methyl-9-azabicyclo[3.3.1]nonanes, 9-oxabicyclo[3.3.1]nonanes, and 9-thiabicyclononanes with bridgehead substituents are interpreted. Heteroatom bridgehead substituents cause downfield shifts of the resonances for γ-anti carbons 3, 5, and 7 in agreement with previous results for bridgehead substituents and in contrast to the upfield γ-anti shifts induced by heteroatoms in monocycles. Equatorial tertiary hydroxyl groups in cyclohexanols cause downfield shifts of the γ-anti carbons.

Within the last several years, ^{13}C NMR spectroscopy has emerged as a very powerful tool for structural analysis in organic chemistry.[1] The power of this technique derives in large measure from several empirically determined, rather well-ordered types of effects exerted by substituents on the chemical shifts of the various carbon atoms in a particular molecule. For example, it has been demonstrated on numerous occasions that a carbon atom disposed γ-gauche to a methyl group resonates at a relatively higher magnetic field than when it is located γ-gauche to a hydrogen or γ-anti to a methyl group.[2] Steric interactions are usually cited as being responsible for such *upfield* shifts. Interestingly, it has also been found that downfield shifts are observed when the encumbered carbon is separated from its steric antagonist by four bonds.[3] While the experimentally obtained γ and δ "steric" shifts are opposite in direction (thus indicating that the shielding mechanisms include significant contributions from terms of other than a steric nature), their individual consistencies render them very valuable in stereochemical assignments.

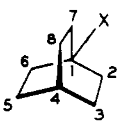
Recently, Eliel and co-workers have disclosed their intriguing findings related to the upfield chemical shifts observed for carbon nuclei γ to a heteroatom.[4] Briefly, their data have confirmed that a *gauche heteroatom* (N, O, F, S, Cl) produces an upfield (steric) shift of a ^{13}C NMR signal *greater* than the upfield shift caused by a gauche carbon group

Table I. Carbon-13 Chemical Shifts for 1-Substituted Bicyclo[3.3.1]nonanes[a,b]

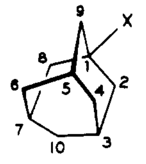
Nucleus	Substituent	C-1	C-2(8)	C-3(7)	C-4(6)	C-5	C-9
	8a, X = H	28.2	31.9	22.8	31.9	28.2	35.2
	8b, X = OH	69.2	39.7	23.1	30.3	32.3	43.6
	8c, X = Cl	71.8	42.1	24.5	29.8	32.9	46.0
	8d, X = CO_2H[c]	41.0	33.2	22.0	30.4	28.0	36.0
	9a, X = H	52.3	26.4	20.4	26.4	52.3	40.9[d]
	9b, X = OH	82.5	33.8	22.0	25.6	57.6	34.2[d]
	9c, X = Cl	90.6	37.6	23.1	25.3	58.9	37.6[d]
	10a, X = H	66.5	29.3	18.8	29.3	66.5	
	10b, X = OH	94.0	36.3	20.6	28.4	72.4	
	10c, X = Cl	99.9	40.2	21.7	27.8	74.2	
	11a, X = H	65.0	27.2	18.4	27.2	65.0	53.0[d]
	11b, X = Cl	93.8	38.8	22.0	26.6	73.3	50.2[d]
	12a, X = H	33.2	32.1	21.6	32.1	33.2	
	12b, X = OH	76.9	41.1	23.4	30.8	40.8	

[a] Expressed in parts per million. [b] Compounds 8–10 measured in $CDCl_3$ with internal Me_4Si; compound 11 measured in D_2O with external $NaO_3S(CH_2)_3Si(CH_3)_3$. [c] Signal for CO_2H, 185.9. [d] Chemical shift for NCH_3.

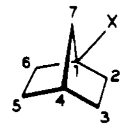
(methyl or methylene); moreover, their investigation has demonstrated that a carbon atom situated γ-anti to a *second row heteroatom* (N, O, F) generally resonates at a significantly higher field than a carbon nucleus located γ-anti to a methyl or methylene group or to a third row heteroatom (S, Cl). As pointed out by Eliel et al., the only exceptions at that time[5] to the shielding γ-anti effects occurred in systems having the heteroatom attached to a bridgehead carbon as reported by Maciel and co-workers for the bicyclo[2.2.2]octane (1) and adamantane (2) frameworks.[8] Subsequent to Eliel's survey,[4] the ^{13}C NMR spectra of some bridgehead functionalized derivatives in the bicyclo[2.2.1]heptane nucleus [i.e., norbornanes (3),[9a] tricyclenes (4),[9b] camphenes (5a),[9c] camphors (5b),[9d] and camphenilones (5c)[9e]] have been studied; both downfield and upfield γ-anti shifts were observed with these substrates. Also, the conversion of α-isospartein (6a) to 7-hydroxy-α-isospartein (6b) results in a 1.3-ppm upfield shift of the bridgehead carbon (9).[10,11]



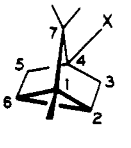
1



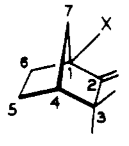
2



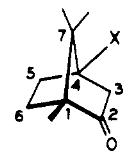
3



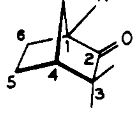
4



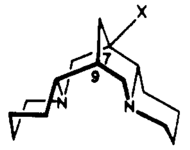
5a



5b



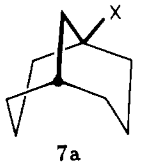
5c



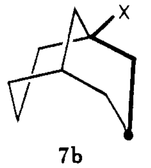
6a: X = H
6b: X = OH

Significantly, all the compounds in Eliel's survey[4] have the heteroatom attached to primary or secondary carbon atoms. By necessity, all bridgehead substituents are attached to tertiary carbons. The following data indicate that changing from primary or secondary substrates to tertiary compounds reverses the direction of the γ-anti effect for monocyclic systems also.

In order to gain additional information pertaining to the directions and magnitudes of the γ-anti effect of bridgehead substituents we have measured the magnetic resonances of the carbon atoms of a few 1-substituted bicyclo[3.3.1]nonanes. In addition, we have studied the ^{13}C NMR of several substrates with a heteroatom (N, O, S) incorporated into the molecular framework at the 9 position of the bicyclo[3.3.1]nonane system.[6,12] The heterobicyclic materials were chosen for study in order to ascertain whether or not the ring heteroatom (which is part of the antiperiplanar arrangement; see formula 7a) would alter significantly the γ-anti effects found for the parent carbobicyclic counterparts. Furthermore, the bicyclo[3.3.1]nonane geometry contains a second γ-anti arrangement (see structure 7b) which, because of differences in bond angles and lengths,[13] could give rise to γ-anti effects different from those exhibited by 7a.



7a



7b

Results and Discussion

Table I collects the chemical shift data for the various 1-substituted bicyclo[3.3.1]nonanes we have examined. The assignments of the chemical shifts are based on the relative intensities of certain signals, splitting patterns observed with fully coupled spectra, and general, well-documented substituent effect trends.[1] Table II lists the specific effects of bridgehead substituents on the chemical shifts of the carbon atoms.

Carbobicyclic Compounds. The conversion of hydrocarbon 8a to bridgehead alcohol 8b results in carbon 5 being deshielded by 4.1 ppm while carbon 3(7) is shifted downfield by only 0.3 ppm. Likewise, the transformation of 8a to chloride

Table II. Bridgehead Substituent Effects for Bicyclo[3.3.1]nonanes[a,b]

Compd	Function	C-1	C-2(8)	C-3(7)	C-4(6)	C-5	C-9
8b	OH	41.0	7.8	0.3	−1.6	4.1	8.4
8c	Cl	43.6	10.2	1.7	−2.1	4.7	10.8
8d	CO_2H	12.8	1.3	−0.8	−1.5	−0.2	0.8
9b	OH	30.2	7.4	1.6	−0.8	5.3	-6.7^c
9c	Cl	38.3	11.2	2.7	−1.1	6.6	-3.3^c
10b	OH	27.5	7.0	1.8	−0.9	5.9	
10c	Cl	33.4	10.9	2.9	−1.5	7.7	
11b	Cl	28.8	11.6	3.6	−0.6	8.3	-2.8^c
12b	OH	43.7	9.0	1.8	−1.3	7.6	

[a] Chemical shifts for substituted compound minus chemical shifts for parent, expressed in parts per million. [b] Negative values indicate upfield shifts. [c] For NCH_3.

Table III. Survey of γ-Anti Effects of Bridgehead Substituents[a,b]

	Type I[c]				Type II[c]				
Compd	Carbon	X = OH	X = Cl	X = CO_2H	Carbon	X = OH	X = Cl	X = CO_2H	Ref
1					3(5,8)	0.4	2.2	−1.5	8
2	3(5,7)	4.1	4.7	−0.2					8
3	4	−1.6	−1.6	1.4	3(5)	0.5	1.1	0.2	9a
4	1	3.5	1.2	1.7					9b
4	2(6)	−1.4	−1.3	−1.0					
5a	4	−2.9	−2.1	0.4	3	0.3	1.0	1.2	9c
5a					5	1.1	1.9	0.7	
5b	1	1.1	0.5	−0.9	2	−2.7	−5.6	−2.7	9d
5b					6	−2.0	−1.3	−0.8	
5c	4	−4.1	−2.6	−0.9	3	−0.6	0.4	1.2	9e
5c					5	5.2	8.7	3.7	
8	5	4.1	4.7	−0.2	3(7)	0.3	1.7	−0.8	

[a] Expressed in parts per million. [b] Negative values indicate upfield shifts. [c] See text for explanations of types.

8c produces downfield shifts of 4.7 and 1.7 ppm for carbons 5 and 3(7), respectively. Thus, it appears that the type of γ-anti arrangement (i.e., **7a** or **7b**) can be important. For convenience the γ-anti effect produced by the arrangement depicted in **7a** is classified as *type I* (the γ-anti carbon is a bridgehead carbon) while the γ-anti effect corresponding to **7b** is defined as *type II* (the γ-anti carbon is not a bridgehead carbon). To help visualize how the two types of γ-anti effects found for alcohol **8b** and chloride **8c** relate to the results of previous reports dealing with bridgehead substituted carbobicyclic systems, Table II has been assembled. First of all, it is interesting to note that the type I γ-anti effects for the very similar frameworks adamantane (**2**) and bicyclo[3.3.1]nonane (**8**) are *identical* (as are the corresponding α and β substituent effects[8b]). Perhaps this fact indicates that the small differences in the pertinent corresponding bond angles or bond distances are inconsequential in the transmission of the γ-anti substituent effect. The other type I effects shown in Table III are mostly shielding. Perhaps the change in direction of the γ-anti effects of the bicyclo[2.2.1]heptane substances (**3–5**) compared to the bicyclo[3.3.1]nonane substrates (**2** and **8**) reflects the substantial difference in CCC angle at the carbon joining the bridgehead carbons: 93.1° in the case of **3** (X = H) and 111.3° for **8a**.[13] However, the tricyclene system (**4**) remains anomalous even though it is geometrically similar to the norbornane skeleton.[13b] Clearly, more data are needed before a general explanation of the type I γ-anti effect can be advanced reliably. On the other hand, there does seem to be a unifying trend for the type II γ-anti effects: for the hydroxy and chloro substituents the shifts are generally deshielding, with a chlorine producing a shift about 1 ppm greater in magnitude than a hydroxyl group.

Heterobicyclic Materials. Previous reports on 9-heterobicyclo[3.3.1]nonanes have not considered the effects of bridgehead functionality on the chemical shifts of the carbons comprising the bicyclic systems.[6,12a–c,e] Examination of the data contained in Tables I and II reveals some interesting trends. Again, the type I γ-anti effects are substantially greater in magnitude than the type II γ-anti effects. For the bridgehead hydroxy derivatives the differences between the type I and type II γ-anti effects are 3.7 ppm for the 9-aza skeleton (**9**), 4.1 ppm for the 9-oxa skeleton (**10**), and 4.8 ppm for the 9-thia skeleton (**12**). These values compare favorably with the related difference of 3.9 ppm found for the carbobicyclic system (**8**). For the bridgehead chloro substrates the differences between the type I and type II γ-anti effects are slightly larger than those found for the hydroxy derivatives (3.9 ppm for **9c** and 4.8 ppm for **10c**) and are somewhat greater than that found for the carbobicyclic system (3.0 ppm for **8c**). An attractive rationalization of the observed differences in the magnitudes of the type I and type II γ-anti effects is based upon the geometrical freedom of the bicyclo[3.3.1]nonane framework: the type I arrangement (**7a**) allows only for bond angle and/or bond length changes, but no changes in the dihedral angle formed by the two planes X–C(1)–C(9) and C(1)–C(9)–C(5) which must remain near 180°. However, for the type II arrangement (**7b**), the dihedral angle formed by the planes X–C(1)–C(2) and C(1)–C(2)–C(3) can vary. In fact, for most of the compounds we report this angle is probably less than 180° due to flattening of the six-membered rings to relieve the C(3)–C(7) steric interactions.[13a] Interestingly, the cationic nature of the *N,N*-dimethylazonia derivative **11b** appears to have little effect on the difference between the type I and type II effects relative to the parent *N*-methylamine derivative **9c** (4.7 vs. 3.9 ppm, respectively).

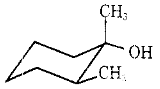
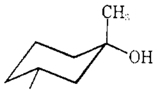
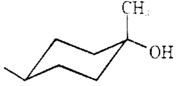
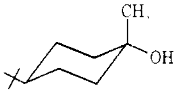
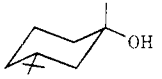
Analysis of the data on the type I and type II γ-anti effects

Table IV. Differences in Bridgehead Substituent Effects between Corresponding 9-Heterobicyclo[3.3.1]nonanes and Bicyclo[3.3.1]nonanes[a]

Entry	Comparison	C-1 (α)	C-2(8) (β)	C-3(7) (γ-II)	C-4(6) (δ)	C-5 (γ-I)
1	**9b–8b**	−10.8	−0.4	1.3	0.8	1.2
2	**9c–8c**	−5.3	1.0	1.0	0.5	1.9
3	**10b–8b**	−13.5	−0.8	1.5	0.7	1.8
4	**10c–8c**	−10.2	0.7	1.2	0.6	3.0
5	**11b–8c**	−14.8	1.4	1.9	1.5	3.6
6	**12b–8b**	2.7	1.2	1.5	0.3	3.5

[a] Substituent effects for the 9-heterobicyclo[3.3.1]nonanes minus the substituent effects for the bicyclo[3.3.1]nonanes expressed in parts per million.

Table V. γ-Anti Effects for Tertiary Hydroxyl Groups

Compd	δ^a	Reference		γ effect		Item
		δ(CH$_3$ ref)^b	δ(H ref)^c	CH$_3$ ref^d	H ref^e	
	C-3 32.2^f	31.9^g	32.1^g	0.3	0.1	1
	C-5 24.3^f	23.4^g	24.3^g	0.9	0.0	2
	C-3 30.6^f	28.9^g	27.6^g	1.7	3.0	3
	C-5 23.8^f	23.2^g	21.3^g	0.6	2.5	4
	C-3,5 32.4^f	i	31.5^h	i	0.9	5
	C-3,5 25.1^f	i	22.6^h	i	2.5	6
	C-3 45.8^f	i	43.4^h	i	2.4	7
	C-5 24.0^f	i	22.3^h	i	1.7	8

[a] Chemical shift, parts per million from Me$_4$Si, of designated carbon. [b] Chemical shift, parts per million from Me$_4$Si, of designated carbon in reference compound wherein the OH group is replaced by CH$_3$. [c] Chemical shift, parts per million from Me$_4$Si, of designated carbon in reference compound wherein the OH group is replaced by H. [d] γ-Anti effect, parts per million, relative to CH$_3$ reference compound. [e] γ-Anti effect, parts per million, relative to H reference compound. [f] Reference 15. [g] From Table 3.5, p 65, ref 1, based on primary data reported in ref 2b. [h] Calculated values for standard compounds obtained as described in ref 4, footnote 24. [i] The γ-anti effects relative to CH$_3$ are not entered in the table for items 5–8. The calculated resonances of the pertinent carbons in the CH$_3$ reference compounds would be the same as for the H reference compounds since the effect of an equatorial methyl group on the γ ring methylene is negligible. Accordingly, the calculated γ-anti effects will be the same for both reference series.

from the viewpoint of comparing directly the heterobicyclic and carbobicyclic materials indicates that the heterobicyclic compounds show consistently greater deshielding effects than the corresponding carbobicyclic substrates (Table IV). The other comparisons assembled in Table IV show that the α effects of the carbobicyclics are substantially more deshielding than the heterobicycles, except for sulfur; the β effects are slightly more deshielding in the case of a bridgehead hydroxy substituent and slightly less deshielding with a bridgehead chloride atom; the δ effects of the carbobicyclic compounds are all slightly less deshielding than those of the heterobicyclic substances.

Conclusions and Comparisons with Monocyclic Compounds. The consistency of our results for the substituent effects in these bicyclic compounds is quite good. In particular, replacement of a bridgehead hydrogen with chlorine or hydroxyl causes a downfield shift in the resonances of carbons 3, 5, and 7. In a single example a bridgehead carboxyl group causes a slight upfield shift of the resonances of these carbons.[14]

Since the shifts caused by bridgehead hetero substituents are opposite in direction to those caused by the same functions in monocyclic systems, we must inquire of the reasons for the difference. The key parameter seems to be the degree of substitution of the carbon bearing the hetero substituent. Every example in the survey of γ-anti effects in monocyclic systems[4] has the hetero substituent placed on a primary or secondary carbon. By necessity all examples of bridgehead substituted compounds have the hetero function on a tertiary carbon. Recently, Senda et al. have analyzed the ^{13}C NMR spectra of some tertiary cyclohexanols. Selected compounds from their study form the basis of Table V. The chemical shifts of carbon atoms γ-anti to an equatorial hydroxyl group are compared to the chemical shifts of the analogous carbons in hydrocarbons wherein the hydroxyl function is replaced by hydrogen or methyl.

The γ-anti effects recorded for items 1–4 are based entirely on measured literature values. Those in items 5–8 are based on literature values for the alcohols[15] but calculated values for the reference compounds, as was the practice in the earlier survey of γ-anti effects.[4] The alcohols are drawn in their predominant conformations.[15]

The γ-anti effects for the set of alcohols in Table V are uniformly downfield, except for item 2 (H reference), which is zero. Accordingly, the degree of substitution of the functionalized carbon is an important factor in determining the direction of the γ-anti effect for hydroxyl. Hydroxy groups in tertiary cyclohexanols and chloro and hydroxy groups at the bridgeheads of bicyclic and tricyclic ring systems usually cause downfield shifts of the the resonances of γ-anti carbon atoms. Further examples will be required to determine the generality and reliability of this phenomenon.[20]

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.[16] Compounds 8–10 were run in $CDCl_3$ solution with internal Me_4Si; compounds 11 were run in D_2O solution with external $NaO_3S(CH_2)_3Si(CH_3)_3$. With the exception of **8c**,[17,18] all of the materials employed in this study were available from previous studies or prepared according to literature procedures.[19]

Acknowledgments. This work was supported by a grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No.—**8a**, 280-65-9; **8b**, 15158-56-2; **8c**, 15158-55-1; **8d**, 17530-63-1; **9a**, 491-25-8; **9b**, 56258-84-5; **9c**, 51209-45-1; **10a**, 281-05-0; **10b**, 37996-41-1; **10c**, 40164-34-9; **11a**, 56258-87-8; **11b**, 62067-15-6; **12a**, 281-15-2; **12b**, 50436-34-5.

References and Notes

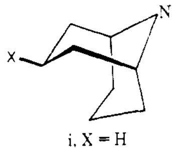
(1) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972; G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley, New York, N.Y., 1972.

(2) (a) D. M. Grant and B. V. Cheney, *J. Am. Chem. Soc.*, **89**, 5315 (1967); (b) D. K. Dalling and D. M. Grant, *ibid.*, **89**, 6612 (1967); (c) *ibid.*, **94**, 5318 (1967); (d) *ibid.*, **96**, 1827 (1974); (e) D. K. Dalling, D. M. Grant, and E. G. Paul, *ibid.*, **95**, 3718 (1973).

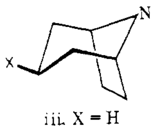
(3) (a) J. J. Kroschwitz, M. Winokur, H. J. Reich, and J. D. Roberts, *J. Am. Chem. Soc.*, **91**, 5927 (1969); (b) S. H. Grover, J. P. Guthrie, J. B. Stothers, and C. T. Tan, *J. Magn. Reson.*, **10**, 227 (1973); (c) J. B. Stothers and C. T. Tan, *Can. J. Chem.*, **52**, 308 (1974); (d) S. H. Grover and J. B. Stothers, *ibid.*, **52**, 870 (1974); (e) J. B. Stothers, C. T. Tan, and K. C. Teo, *ibid.*, **54**, 1211 (1976).

(4) E. L. Eliel, W. F. Bailey, L. D. Kopp, R. L. Willer, D. M. Grant, R. Bertrand, K. H. Christensen, D. K. Walling, M. W. Duch, E. Wenkert, F. M. Schell, and D. W. Cochran, *J. Am. Chem. Soc.*, **97**, 322 (1975).

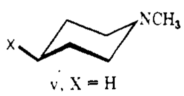
(5) An exception to the upfield γ-anti effect is found in the *N*-methylgranatanine



i, X = H
ii, X = OH



iii, X = H
iv, X = OH



v, X = H
vi, X = OH

sytem i. ^{13}C NMR data reveal that on going from i to ii the bridgehead carbon atoms (which are situated in an anti-periplanar arrangement to the 3-*exo*-hydroxy group) experience a *downfield* shift of 1.6 ppm; for the corresponding quaternary methochlorides a downfield shift of 1.3 ppm was observed.[6] In contrast with the above findings are the data for the transformation of iii to iv and the conversion of v to vi for which the analogous carbons show shifts of −1.1 and −3.0 ppm, respectively.[7]

(6) J. R. Wiseman and H. O. Krabbenhoft, *J. Org. Chem.*, **40**, 3222 (1975).

(7) (a) E. Wenkert, J. S. Bindra, C. J. Chang, D. W. Cochran, and F. M. Schell, *Acc. Chem. Res.*, **7**, 46 (1974); (b) G. Ellis and R. G. Jones, *J. Chem. Soc., Perkin Trans. 2*, 437 (1972).

(8) (a) G. E. Maciel and H. C. Dorn, *J. Am. Chem. Soc.*, **93**, 1268 (1971); (b) G. E. Maciel, H. C. Dorn, R. L. Green, W. H. Kleschick, M. R. Peterson, Jr., and G. H. Wahl, Jr., *Org. Magn. Reson.*, **6**, 178 (1974).

(9) (a) G. S. Poindexter and P. J. Kropp, *J. Org. Chem.*, **41**, 1215 (1976); (b) D. G. Morris and A. M. Murray, *J. Chem. Soc., Perkin Trans. 2*, 734 (1975); (c) D. G. Morris and A. M. Murray, *ibid.*, 539 (1975); (d) D. G. Morris and A. M. Murray, *ibid.*, 1579 (1976); (e) F. G. Brown and D. G. Morris, *ibid.*, 125 (1977).

(10) F. Bohlmann and R. Zeisberg, *Chem. Ber.*, **108**, 1043 (1975).

(11) For ^{13}C NMR chemical shift data for 4-homotwistane derivatives see (a) N. Takaishi, Y. Imamoto, and K. Aigami, *J. Org. Chem.*, **40**, 276 (1975); (b) N. Takaishi, Y. Fujikura, Y. Inamoto, H. Ikeda, K. Aigami, and E. Osawa, *J. Chem. Soc., Chem. Commun.*, 371 (1975); (c) K. Aigami, Y. Inamoto, N. Takaishi, and Y. Fujikura, *J. Med. Chem.*, **19**, 536 (1976).

(12) (a) J. R. Wiseman and H. O. Krabbenhoft, *J. Org. Chem.*, **41**, 589 (1976); (b) J. R. Wiseman, H. O. Krabbenhoft, and B. R. Anderson, *ibid.*, **41**, 1518 (1976); (c) J. A. J. M. Vincent, P. Schipper, Ae. de Groot, and H. M. Buck, *Tetrahedron Lett.*, 1989 (1975); (d) A. Heumann and H. Kolshorn, *Tetrahedron*, **31**, 1571 (1975); (e) M. Barrelle and M. Apparu, *Tetrahedron Lett.*, 2611 (1976).

(13) (a) E. L. Osina, V. S. Mastryukov, L. V. Viklov, and N. A. Belikova, *J. Chem. Soc., Chem. Commun.*, 12 (1976), and references cited therein; (b) J. F. Chiang, C. F. Wilcox, and S. H. Bauer, *Tetrahedron*, **25**, 369 (1969).

(14) Upfield shifts for carbons located γ-anti to carbomethoxy groups have been observed previously: M. Gordon, S. H. Grover, and J. B. Stothers, *Can. J. Chem.*, **51**, 2092 (1973).

(15) Y. Senda, J. Ishiyama, and S. Imaizumi, *Tetrahedron*, **31**, 1601 (1975).

(16) The ^{13}C NMR spectra of compounds **8c** and **10c** were measured with a Varian XL-100 spectrometer.[17] To ensure that accurate comparisons of the data obtained with the two different instruments could be made, hemiketal **10b** was analyzed with each spectrometer; the corresponding ^{13}C chemical shifts determined for **10b** were identical with each instrument.

(17) We wish to thank Professor W. G. Dauben for providing the sample of **8c** and for his assistance in obtaining the ^{13}C NMR spectra of **8c** and **10c**.

(18) W. G. Dauben and C. D. Poulter, *J. Org. Chem.*, **33**, 1237 (1968).

(19) (a) J. R. Wiseman and W. A. Pletcher, *J. Am. Chem. Soc.*, **92**, 956 (1970); (b) C. B. Quinn, Ph.D. Thesis, University of Michigan, Ann Arbor, Mich., 1973; (c) H. O. Krabbenhoft, Ph.D. Thesis, University of Michigan, Ann Arbor, Mich., 1974; (d) H. O. Krabbenhoft, J. R. Wiseman, and C. B. Quinn, *J. Am. Chem. Soc.*, **96**, 258 (1974).

(20) **Note Added in Proof.** Since submission of this report two related reports have been published: H. Duddeck and P. Wolff, *Org. Magn. Reson.*, **8**, 593 (1976); J. A. Peters, J. M. van der Toorn, and H. van Bekkum, *Tetrahedron*, **33**, 349 (1977).

An Unusual Magnetic Equivalence in the Proton Magnetic Resonance of Dialkylbenzamides

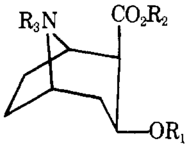
Virgil I. Stenberg,* S. P. Singh, and N. K. Narain

Department of Chemistry, The University of North Dakota, Grand Forks, North Dakota 58202

Received September 28, 1976

N-Benzoylnorecgonine methyl ester, *N*-benzoylpiperidine, and *N,N*-diethylbenzamide exhibit one set of ^1H NMR signals for aromatic protons whereas cocaine and seven other benzoate esters, acetophenone, α,α,α-trimethylacetophenone, α,α,α-trichloroacetophenone, benzamide, and *N*-ethylbenzamide have two sets separated by ca. δ 0.6. The observed unusual magnetic equivalence of the first three compounds is attributed to the steric interaction of the dialkylamine and the phenyl group with the resultant loss of coplanarity between the phenyl and carbonyl functional groups.

During the course of our investigations on the photochemical behavior of cocaine (I),[1] its photoproducts,[2] and related compounds,[3] the aromatic protons of cocaine were observed to occur as two groups of multiplets in the ^1H NMR spectrum at δ 7.93 (m, 2 H) and 7.36 (m, 3 H), whereas the aromatic proton resonances of *N*-benzoylnorecgonine methyl ester (II), cocaine's O → N benzoyl migration–demethylation product, appear as a sharp singlet at δ 7.45, Table I. This investigation examines the reasons for the surprising proton



I, R_1 = COPh; R_2 = CH_3; R_3 = CH_3
II, R_1 = H; R_2 = CH_3; R_3 = COPh
III, R_1 = COPh; R_2 = CH_3; R_3 = H
IV, R_1 = COPh; R_2 = H; R_3 = CH_3