The Geometry of Myrtenal. A Detailed Analysis of the Nuclear Magnetic Resonance Spectrum of a Bicyclo[3.1.1]heptene-2 System

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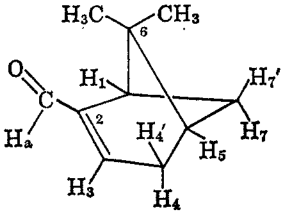
Detailed analyses of nuclear magnetic resonance spectra of myrtenal (I) are reported. The magnitude of spin–spin coupling through two, three, and four bonds is used to define the geometry of the system and is discussed, in part, in terms of bridged cyclobutanes. A large four-bond coupling (5.78 cps) is found between bridgehead protons.

Nuclear magnetic resonance (nmr) spectroscopy has proved to be a unique tool for gaining insight into configuration and bonding in bridged bicyclic systems in solution. In addition, the rigid geometries of these compounds make them ideal model compounds for the study of relationships between geometry and the magnitude of nmr parameters. In recent years, nmr data has been reported for many derivatives of different classes of bicyclic systems, including bicyclo[1.1.0]butanes,[2] bicyclo[1.1.1]pentanes,[2] bicyclo[2.1.1]hexanes,[3] bicyclo[2.2.1]heptanes,[4] bicyclo[3.2.1]- and [2.2.2]octanes,[5,6] and bicyclo[3.2.2]nonanes.[7] A detained analysis of the nmr spectrum of myrtenal (I), a bicyclo[3.1.1]heptene-2 system, was undertaken in an attempt to define the geometry of the system and to elucidate fully the parameters describing the spectrum. Of particular interest was the geometry of the cyclobutane ring relative to other bridged cyclobutanes and the geometry of the C_1, C_2, C_3, C_4, C_5 bridge.



I

Experimental Section

Myrtenal was prepared by the chromic acid oxidation of myrtenol.[8] The desired aldehyde was extracted from the reaction mixture with pentane, distilled (bp 90–95° at 12 mm), and finally purified by vapor phase chromatography (vpc) using a 6-ft-long (0.5-in.-o.d.) column of 10% Carbowax 20M on 30–60 mesh (acid washed) Chromosorb P at 180°. The purity of the final sample was shown to be greater than 99%.

Experimental spectra were obtained on 30% w/v solutions in deuteriochloroform with a Varian HA-100 instrument equipped with a spin decoupler. Theoretical spectra were calculated using a modified form of LAOCOON II.[9]

Results and Discussion

The parameters describing the spectrum of myrtenal with their probable error are summarized in Tables I and II. A comparison of the observed and calculated spectrum of the ring protons is shown in Figure 1. The root–mean–square error over 299 matched lines was 0.139.

TABLE I

CHEMICAL SHIFTS OF PROTONS IN MYRTENAL

Proton	δ, ppm	Probable error, ppm
H_a	9.45	
H_1	2.873	0.017
H_3	6.670	0.013
H_4, $H_{4'}$	2.576	0.019
H_5	2.200	0.014
H_7	1.052	0.018
$H_{7'}$	2.499	0.017
CH_3	1.34, 0.74	

TABLE II

COUPLING CONSTANTS OF PROTONS IN MYRTENAL

Interaction	J, cps[a]	Probable error, cps
$J_{1,3}$	1.488[b]	0.020
$J_{1,4}$	0.0	
$J_{1,4'}$	0.0	
$J_{1,5}$	5.779[b]	0.022
$J_{1,7}$	0.038	0.024
$J_{1,7'}$	5.394	0.025
$J_{3,4}$	3.012	0.023
$J_{3,4'}$	3.048	0.023
$J_{3,5}$	1.505[b]	0.019
$J_{3,7}$	0.0	
$J_{3,7'}$	0.0	
$J_{4,4'}$	0.060[c]	0.022
$J_{4,5}$	2.771	0.028
$J_{4,7}$	0.0	
$J_{4,7'}$	0.0	
$J_{4',5}$	3.066	0.027
$J_{4',7}$	0.0	
$J_{4',7'}$	0.0	
$J_{5,7}$	0.110	0.022
$J_{5,7'}$	5.746	0.022
$J_{7,7'}$	−9.049	0.026

[a] A positive value for all vicinal (three-bond) and a negative value for all geminal (two-bond) coupling interactions was assumed. [b] The sign of the coupling constant was not determined. Variation of the sign had little effect on the calculated spectrum. [c] A good spectral fit was also obtained when a value of −13.00 was used. The closeness of the chemical shifts of H_4 and $H_{4'}$ precluded an accurate measure of the coupling constant.

The singlet at δ 9.45 and the septet at 6.67 are readily assigned to H_a and H_3, respectively, on the basis of their presence on the α,β-unsaturated carbonyl system. In addition, the singlets (equivalent to three

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(1) Public Health Service Predoctoral Fellow, 1965–1967.

(2) K. Wiberg, G. Lampman, R. Ciula, D. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965).

(3) J. Meinwald and A. Lewis, *J. Amer. Chem. Soc.*, **83**, 2769 (1961); K. Wiberg, B. Lowry, and B. Nist, *ibid.*, **84**, 1594 (1962).

(4) K. Ramey, D. Lini, R. Moriarty, H. Gopal, and H. Welsh, *ibid.*, **89**, 2401 (1967), and references therein.

(5) C. Jefford, S. Mahajan, J. Waslyn, and B. Waegell, *ibid.*, **87**, 2183 (1965); C. Jefford, B. Waegell, and K. Ramey, *ibid.*, **87**, 2191 (1965).

(6) K. Tori, Y. Takano, and K. Kitahonki, *Chem. Ber.*, **97**, 2798 (1964).

(7) C. Jefford, S. Mahajan, and K. Ramey, *Chem. Commun.*, 617 (1965).

(8) A. Heritier, *Ann.*, **459**, 171 (1927).

(9) S. Castellano and A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).

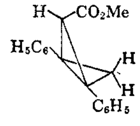
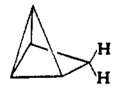
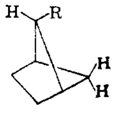
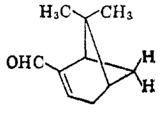
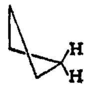
protons each) at δ 1.34 and 0.74 can be attributed to the *gem*-dimethyl group attached to C_6. Six protons remain to be accounted for. Irradiation of the septet at δ 6.67 causes the triplet of doublets at δ 2.87 to collapse to a triplet, the irregular triplet at δ 2.57 to collapse to an irregular doublet, and the multiplet at δ 2.20 to simplify considerably. The olefinic proton, H_3, would be expected to interact only with H_1, H_4, $H_{4'}$, and H_5. Thus the remaining signals at δ 2.49 and 1.05 must be attributed to H_7 and $H_{7'}$. Decoupling of the species at δ 1.05 only effects the signal at δ 2.49. The doublet at δ 1.05 is assigned to H_7 and its high upfield chemical shift results from a strong shielding effect of the π electrons in the α,β-unsaturated carbonyl system. A similar anisotropic shielding effect has been observed for C_6 *endo* protons in a series of 5-substituted bicyclo[2.2.1]heptenes-2.[10]

An expected and observed slight downfield shift of H_1 (tertiary and allylic) relative to the other nonolefinic ring protons facilitates analysis of the remaining part of the spectrum. The triplet of doublets at δ 2.87 is assigned to H_1 and the irregular triplet at δ 2.57 to H_4 and $H_{4'}$. The remaining multiplet at δ 2.20, equivalent to one proton, is attributed to H_5.

Geminal coupling is observed between H_7 and $H_{7'}$ and has a value of -9.0 cps (the negative sign is assigned on the basis of analogy with other geminal couplings). The value of this coupling constant fits a general trend in bridged cyclobutanes[11] where J_{gem} decreases (becomes more negative) as the number of atoms in the bridge increases. This is illustrated by the data in Table III. An increase in the C_5–C_7–C_1 angle and a corresponding decrease in the H_7–C_7–$H_{7'}$ angle in myrtenal would result in a decrease in the amount of s character in the C–H bonds and hence in the geminal coupling constant. The C_5–C_7–C_1 angle in myrtenal is estimated[11] to be approximately 97°.

TABLE III

J_{gem} IN BRIDGED CYCLOBUTANES

Compound	No. of carbons in bridge	J_{gem}, cps	Ref
	0	−1.7	*a*
	1	−3.1	*b*
	2	−5.4 to −8.4	*c*
	3	−9.0	This study
		−12.0 to −15.0	*d*

[a] S. Masamune, *Tetrahedron Lett.*, 945 (1965). [b] G. Closs and R. Larrabee, *ibid.*, 287 (1965). [c] See ref 3. [d] See ref 11.

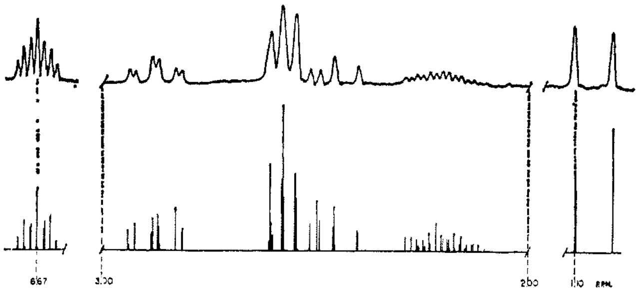
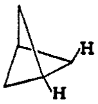
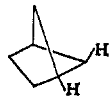
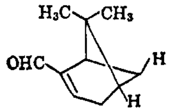


Figure 1.—Experimental and calculated nmr spectrum of the ring protons of myrtenal.

Vicinal couplings of H_7 with H_1 and H_5 are neglible as in the case of similar protons in bicyclo[2.1.1]hexanes[3] and bicyclo[1.1.1]pentanes.[2] On the other hand, the couplings between $H_{7'}$ and the bridgehead protons is larger. A trend is also seen for related vicinal coupling constants in bridged cyclobutanes and is summarized in Table IV. The increase in J_{vic} can be caused by a slightly smaller dihedral angle or more likely by an increase in θ, the angle described by the C–H and C–C bonds,[12] *i.e.*, $H_1C_1C_7$, *etc.*

TABLE IV

J_{vic} IN BRIDGED CYCLOBUTANES

Compound	No of carbons in bridge	J_{vic}, cps	Ref
	1	0	*a*
	2	2	*b*
	3	5.4–5.7	This study

[a] See ref 2. [b] See ref 3.

The remaining vicinal coupling constants arise from interactions among H_3, H_4, $H_{4'}$, and H_5. Using the relationship between dihedral angle and vicinal coupling constants,[12] it can be qualitatively concluded that the dihedral angles relating H_3 with H_4 and H_3 with $H_{4'}$ are very nearly equal. On the other hand, the dihedral angle between $H_{4'}$ and H_5 is slightly smaller than that between H_4 and H_5. This data taken together with the inequality of $J_{17'}$ and $J_{57'}$ show that the five carbons, C_1, C_2, C_3, C_4, and C_5, are not strictly coplanar but somewhat puckered.

Three long-range coupling interactions are present in myrtenal. The sign of the allylic coupling between H_1 and H_3 was not determined but, if it is assumed that the angle between the C_1–H_1 bond and the nodal plane of the C_2–C_3 bond is nearly zero, present theory[13,14] predicts that the π-bond contribution to this coupling will be negligible and the σ contribution will be positive and about 1.3 cps. This conclusion is supported by the near equality of the four-σ-bond coupling between H_3 and H_5 which is also assumed to be positive.[14] The remaining long-range coupling is between H_1 and H_5

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(10) R. G. Foster and M. C. McIvor, *Chem. Commun.*, 280 (1967).

(11) R. Cookson, T. Crabb, J. Frankel, and J. Hudec, *Tetrahedron, Suppl.*, **7**, 355 (1966).

(12) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

(13) E. Garbisch, *ibid.*, **86**, 5561 (1964).

(14) M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1964).

and has an absolute value of 5.78 cps. This coupling interaction was verified by decoupling H_5 from other species and observing the collapse of the triplet of doublets at δ 2.87 to a doublet of doublets. The value of 5.78 cps falls in between 1.5 cps, found for coupling between the bridgehead protons in bicyclo[2.2.1]heptanes, and 18 cps, found for similar coupling in bicyclo[1.1.1]pentane.[2] Presumably, as the bridgeheads are brought closer together by decreasing the number of carbons in the intervening bridges, the interaction between bridgehead protons is enhanced.

Registry No.—Myrtenal, 564-94-3.

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[15] R. B. Bates and V. P. Thalacker, *J. Org. Chem.*, **33**, 1730 (1968).

Nuclear Magnetic Resonance Spectral Parameters in Bicyclo[3.1.1]heptanes. α-Pinene, Myrtenal, and Verbenone

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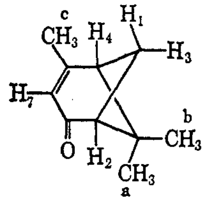
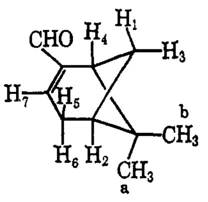
Nmr spectral parameters are derived for three bicyclo[3.3.1]heptane derivatives. As expected, the coupling constants vary little among the three compounds. A four-bond coupling constant of from +5.9 to +6.4 cps was observed between the bridgehead protons in these compounds, and two five-bond couplings of ±1.8 cps were found in α-pinene (III).

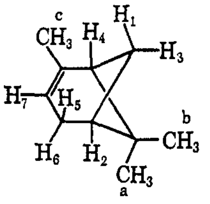
Among the bicyclo[3.1.1]heptanes are members of the pinene family of naturally occurring terpenoids. This paper concerns three of these compounds, verbenone (I), myrtenal (II), and α-pinene (III), the latter of which is the most abundant natural cyclobutane. A set of chemical shifts and coupling constants which fits the nmr spectrum of each of these compounds has been found and is given in Tables I and II. As is evident from Table II, the coupling constants hold very well from compound to compound in this series, and should prove useful in the analysis of other bicyclo[3.1.1]heptanes.



I



II



III

The nmr spectra of related compounds containing cyclobutane rings, including bicyclo[2.1.1]hexanes,[1] bicyclo[1.1.1]pentanes,[2] and tricyclo$[1.1.1.0^{4,5}]$pentanes,[3] have previously been analyzed. Bicyclo[2.2.1]heptanes, isomeric with the [3.1.1]heptanes, have been studied extensively.[4] In some of these compounds, long-range couplings (through more than three bonds) have been observed.[5] Some progress has been made in developing the theory of long-range coupling,[6] but a thorough understanding awaits the measurement of more such couplings in compounds of known molecular geometry such as the ones reported herein.

Table I

Chemical Shifts (τ) at 100 Mc

Proton	I	II	III
CH_3-a	9.00	9.26	9.16
CH_3-b	8.52	8.67	8.74
CH_3-c	8.00		8.35
H_1	7.94	8.96	8.84
H_2	7.38	7.80	7.92
H_3	7.22	7.51	7.66
H_4	7.60	7.12	8.06
H_5, H_6		7.43	7.79, 7.81
H_7	4.27	3.29	4.88
CHO		0.48	

Table II

Coupling Constants (in Cycles per Second)

	I	II	III
J_{12}	0.32^{a}	0.3	0.3
J_{13}	-9.08^{a}	−8.9	−8.5
J_{14}	0.04^{a}		
J_{23}	5.53^{a}	5.9	5.7
J_{24}	$6.50^{a,b}$	$5.9^{c,b}$	5.9^{b}
J_{25}		3.0	2.8
J_{26}		3.0	2.8
J_{27}	$1.41^{a,b}$	1.4^{d}	1.4^{d}
J_{34}	5.90^{a}	5.7	5.7
J_{37}	0.11^{a}		
J_{47}	$1.32^{a,b}$	$1.4^{c,b}$	1.4^{b}
J_{56}		*d*	*d*
J_{57}		3.0	2.8
J_{67}		3.0	2.8
$J_{C\text{-}5}$			1.8^{b}
$J_{C\text{-}6}$			1.8^{b}
$J_{C\text{-}7}$	−1.5		−1.5

[a] Results from least-squares refinement using LAOCOON II, part II. [b] Sign based on calculations by M. Barfield and J. Reed, private communications, University of Arizona, 1967. [c] Sign verified by spin tickling. [d] Spectrum insensitive to this constant.

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[1] J. Meinwald and A. Lewis, *J. Amer. Chem. Soc.*, **83**, 2769 (1961); K. B. Wiberg, B. R. Lowry, and B. J. Nist, *ibid.*, **84**, 1594 (1962).

[2] K. Wiberg, *et al.*, *Tetrahedron*, **21**, 2749 (1965).

[3] S. Masamune, *J. Amer. Chem. Soc.*, **86**, 735 (1964).

[4] K. C. Ramey, D. C. Lini, R. M. Moriarty, H. Gopal, and H. G. Welsh, *ibid.*, **89**, 2401 (1967), and references therein.

[5] S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

[6] (a) M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1964); (b) *ibid.*, **46**, 811 (1967).