^{13}C Chemical Shifts of 1-Substituted Camphenes

By **David G. Morris** * and **A. Malcolm Murray,** Department of Chemistry, University of Glasgow, Glasgow G12 8QQ

^{13}C Chemical shifts of a series of 1-substituted camphenes (1)—(10) are reported. Whereas low-field β-shifts for C(6) and C(7) exhibit normal behaviour for secondary carbons in bridgehead substituted fused ring systems, more strongly electron-withdrawing substituents bring about greater upfield shifts for the *sp*^{2} hybridised β-C(2). In the 1-hydroxymethyl derivative (6) the presence of intramolecular hydrogen bonding does not bring about a low field shift for C(2).

PREVIOUSLY ^{13}C chemical shifts of bridgehead substituted bicyclic and tricyclic compounds have been examined in order to investigate factors which influence chemical shift variation in alicyclic systems.[1-4] Camphenes (1)—(10), substituted at C(1), in general form synthetic precursors of 4-substituted tricyclenes previously studied and, with the different substituent pattern, form a relevant series for investigation of ^{13}C substituent effects.

Assignments of ^{13}C absorptions of camphenes (1)—(10) were made by consideration of the chemical shifts in conjunction with the off-resonance spectra. Throughout this series little problem is caused by overlapping of signals of like off-resonance multiplicity.

---

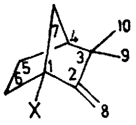
[1] T. Pehk, E. Lippmaa, V. V. Sevostjanova, M. M. Krayushkin, and A. I. Tarasova, *Org. Magnetic Resonance*, 1971, **3**, 783.

[2] J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, **92**, 7107.

[3] G. E. Maciel and H. C. Dorn, *J. Amer. Chem. Soc.*, 1971, **93**, 1268.

[4] D. G. Morris and A. M. Murray, *J.C.S. Perkin II*, in the press.

Support for the assignment of C(7) is provided by consideration of the exact triplet observed in the off-resonance spectrum in relation to the additional fine structure for C(5) and C(6).[5] ^{13}C Chemical shifts of camphenes (1)—(10) are reported in Table 1 and in Table 2 are presented the derived chemical shift increments.



(1) X = H
(2) X = Me
(3) X = NH_2
(4) X = OH
(5) X = Cl
(6) X = CH_2OH
(7) X = CO_2H
(8) X = $CONH_2$
(9) X = CO_2Me
(10) X = NO_2

In relation to other bridgehead substituted bicyclic[1,3,4] and tricyclic[4] systems the substituent-bearing C(1) of the camphenes absorbs at lower field on account of the electron-withdrawing character of the exocyclic double bond; however the low field α-shifts of camphenes (1)—(10) are of comparable magnitude to those of related systems,[1-4] and empirically correlate well with the electronegativity parameter E_R[6] (r 0·984).

The secondary β-carbons C(6) and C(7) respond similarly to variation of substituent character and for both the largest β-shifts are given by Class I substituents[1] which contain not more than one atom heavier than hydrogen. Where the substituents contain more than one atom heavier than hydrogen, Class II substituents,[1] the smaller β-shifts exhibited by C(6) with respect to C(7) are rationalised in terms of the greater distance over which the shielding attributed to the second ' heavy ' atom [β to the C(1) bridgehead] of the substituent must act in the case of the more ' tied back ' carbon C(7). In a wider context the low field β-shift sequence, exemplified for the case of a nitro-substituent, 3·90 [C(3), C(5) tricyclene[4]] > 3·69 [C(7) camphene] > 3·30 [C(6) camphene] > 2·80 p.p.m. [C(2) adamamtane[1]] may be rationalised on similar grounds. It is assumed that the geometry of the fused ring systems is not perturbed by changes of substituent character. Accordingly these shielding effects brought about by *e.g.* the oxygen of the nitro-group in (10) which is now γ to C(6) and C(7) in 1-substituted camphenes appear to be, at least partially, similar to the normal shielding of carbons by γ-substituents.[7,8]

TABLE 1

^{13}C Chemical shifts of 1-substituted camphenes (p.p.m.)

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)
H	48·2	165·9	41·7	47·0	23·8	28·9	37·4	99·1	29·4	25·8		
CH_3	49·9	169·2	42·8	47·4	25·5	35·6	44·3	96·8	29·6	26·1	18·3	
NH_2	66·5	168·2	42·4	45·5	25·3	35·3	45·5	97·2	29·6	26·3		
OH	84·7	165·9	42·0	44·1	24·9	33·6	43·4	97·7	29·4	26·3		
Cl	73·4	163·0	42·7	44·9	25·7	37·9	46·3	101·3	29·8	26·3		
CH_2OH	56·2	165·2	43·3	47·0	24·6	31·0	39·6	98·3	29·2	25·9	63·8	
CO_2H	59·5	162·4	42·9	47·4	24·5	31·9	40·7	101·0	29·6	26·0	180·7	
$CONH_2$	60·7	163·9	43·0	47·7	24·6	31·4	41·6	101·0	29·6	26·0		
CO_2CH_3	59·7	163·0	42·8	47·3	24·5	31·9	40·6	100·6	29·6	26·0	174·1	47·3
NO_2	96·2	158·8	43·0	44·7	24·7	32·2	41·1	101·0	29·6	26·1		

TABLE 2

^{13}C Chemical shift increments of 1-substituted camphenes (p.p.m.)

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)
H	0	0	0	0	0	0	0	0	0	0
CH_3	1·7	3·3	1·1	0·4	1·7	6·7	6·9	−2·3	0·2	0·3
NH_2	18·3	2·3	0·7	−1·5	1·5	6·4	8·1	−1·9	0·2	0·5
OH	36·5	0·0	0·3	−2·9	1·1	4·7	6·0	−1·4	0·0	0·5
Cl	25·2	−2·9	1·0	−2·1	1·9	9·0	8·9	2·2	0·4	0·5
CH_2OH	8·0	−0·7	1·6	0·0	0·8	2·1	2·2	−0·8	−0·2	0·1
CO_2H	11·3	−3·5	1·2	0·4	0·7	3·0	3·3	1·9	0·2	0·2
$CONH_2$	12·5	−2·0	1·3	0·7	0·8	2·5	4·2	1·9	0·2	0·2
CO_2CH_3	11·5	−2·9	1·1	0·3	0·7	3·0	3·2	1·5	0·2	0·2
NO_2	48·0	−7·1	1·3	−2·3	0·9	3·3	3·7	1·9	0·2	0·3

By way of contrast β-shifts of the sp^2 C(2) are to high field in camphenes (1)—(10), with magnitudes such as to give an empirical correlation with the linear free energy parameter σ_I; in particular no dependence of the magnitude of the β-shifts with the number of non-hydrogen atoms of the C(1) substituent is observed. A further point of interest occurs in respect of the C(2) β-shift in the hydroxymethyl derivative (6) where high dilution i.r. spectral measurements indicate partial intramolecular hydrogen bonding of the hydroxy-group; this hydrogen bonding is of the $\pi \cdots$H–O type. No such hydrogen bonding was shown by (4) where an unfavourable geometry exists and we were unable to obtain evidence from the i.r. spectra of (7) for the presence of intramolecular hydrogen bonding. The upfield β-shift of C(2) in (6) is in contrast to the

---

[5] J. B. Grutzner, *J.C.S. Chem. Comm.*, 1974, 64.

[6] J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, 1961, **34**, 1099.

[7] J. B. Stothers, C. T. Tan, and K. C. Teo, *Canad. J. Chem.*, 1973, **51**, 2893.

[8] E. Lippmaa, T. Pehk, and J. Paasivirta, *Org. Magnetic Resonance*, 1973, **5**, 277.

low-field shifts[9] of *ca.* 7 p.p.m. observed for the carbonyl carbons of *e.g. ortho*-substituted acetophenones[10] where hydrogen bonding occurs with non-bonded electrons on oxygen. It is possible that in (6) a situation obtains where the high-field β-shift of C(2) is a composite effect containing a low-field component on account of hydrogen bonding, although it is possible that at the higher concentrations and in the different solvent of the n.m.r. experiment, the role of an intramolecularly hydrogen bonded component of (6) is minimised.

Small low-field γ-shifts are observed for secondary C(5) and quaternary C(3), and the values may be sorted approximately with regard to whether the C(1) substituent contains one or more atoms heavier than hydrogen. Throughout the series (1)—(10), C(5) has the highest field absorption; this is brought about[8] by a *ca.* 8 p.p.m. upfield shift attributable to the C(9) *endo*-methyl. C(5) γ-Shifts show a broadly similar response to substituent variation as C(6) β-shifts. The exocyclic sp^2 C(8) show γ-shifts which are of a novel type.

Chemical shifts of the remaining carbons, C(4) and the exocyclic methyl groups C(9) and C(10) show irregular or small variations with substituent character.

The present ^{13}C chemical shift data on 1-substituted camphenes indicate by comparison with other fused ring structures, that it is possible to translate both α- and β-shifts at secondary carbons into related systems, after modification where necessary,[11] with reasonable confidence. However substituent-induced shifts at carbons more remote from the substituent are dependent on the nature of the ring system as well as the hybridisation type and ring substituent pattern. The latter two points are illustrated for C(3), C(5), and C(8) of 1-substituted camphenes whose γ-shifts show individual dependence on substituent character. A comparison of C(2), C(6), and C(7) β-shifts indicates that the hybridisation is also an important factor here.

EXPERIMENTAL

^{13}C N.m.r. spectra were obtained at natural abundance with a Varian XL 100 spectrometer operating in the pulse Fourier transform mode. Spectra were determined with deuteriochloroform solutions containing tetramethylsilane as an internal standard. Proton-noise decoupling was carried out with a wideband noise decoupler; probe temperature was *ca.* 35°. The spectra were recorded at the University of Edinburgh under the S.R.C. Fourier transform service.

I.r. spectra were determined with a Perkin-Elmer 227 spectrophotometer.

Camphene was a commercial sample. The remaining camphenes were obtained by literature methods: (2), (6);[12] (3), (4);[13] (5);[14] (7)—(9);[15] (10).[16] 1-Hydroxymethylcamphene (6) showed $\nu_{max.}$ (CCl_4; 0·05M) 3639 (free OH) and 3600 cm^{-1} (intramolecular hydrogen bonded OH). 1-Hydroxycamphene (4) showed $\nu_{max.}$ (CCl_4; 0·05M) 3605 cm^{-1}.

We are grateful to the S.R.C. for a maintenance award (to A. M. M.) and to Dr. A. B. Boyd for determination of ^{13}C spectra.

[4/1897 *Received*, 17*th September*, 1974]

---

[9] J. B. Stothers, 'Carbon-13 N.M.R. Spectroscopy,' Academic Press, London, p. 494 *et seq.*

[10] G. E. Maciel and G. B. Savitsky, *J. Phys. Chem.*, 1964, **68**, 437.

[11] T. Pehk, M. Alla, and E. Lippmaa, *Org. Magnetic Resonance*, 1973, **5**, 351.

[12] W. Z. Antkowiak, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, 1966, **14**, 437 (*Chem. Abs.*, 1967, **66**, 18,768d).

[13] A. Nickon, T. Nishida, J. Frank, and R. Muneyuki, *J. Org. Chem.*, 1971, **36**, 1075.

[14] P. Lipp and H. Knapp, *Chem. Ber.*, 1940, **73**, 915.

[15] S. A. Sherrod, R. G. Bergmann, G. J. Gleicher, and D. G. Morris, *J. Amer. Chem. Soc.*, 1972, **94**, 4615.

[16] Y. Brunel, H. Lemaire, and A. Rassat, *Bull. Soc. chim. France*, 1964, 1895.