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NOTE

^{17}O NMR Spectra of 2-Phenylmethylene Cyclic Ketones

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Natural abundance ^{17}O NMR spectra of some 2-phenylmethylene cyclic ketones are reported. The ^{17}O shifts vary with the ring system, and correlate well with those of the corresponding cyclic ketones. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

α,β-Unsaturated ketones are important organic derivatives which have been extensively studied and which have found a broad application in synthesis.[1] Numerous spectroscopic studies have been devoted to these compounds employing, e.g., ^{1}H and ^{13}C NMR, UV and IR spectroscopy.[1] The ^{17}O spectra of some α,β-unsaturated carbonyl compounds have been reported.[2,3] Most of them are concerned with the β-substituents. This paper describes a study of the influence of ring systems on the ^{17}O chemical shifts of the carbonyl O atoms of 2-phenylmethylene cyclic ketones.

RESULTS AND DISCUSSION

The ^{17}O chemical shifts for the 2-phenylmethylene cyclic ketones **1b**–**9b** are summarized in Table 1. The ^{17}O signals of the carbonyls of these compounds appear between 459 and 538 ppm. They are downfield (26–44 ppm) of those of the corresponding cyclic ketones (**1a**–**9a**)[4] and upfield (60–105 ppm) of those of the corresponding enaminones (**1c**–**9c**).[4] The ^{17}O NMR spectra of **2a**, **2b** and **2c** are shown in Fig. 1. A similar trend, but much smaller, was noted for the ^{13}C shift values of

Table 1. ^{17}O and ^{13}C chemical shifts (δ, ppm) of the respective C=O groups for the cyclic ketones 1a–9a, 2-phenylmethylene cyclic ketones 1b–9b and 2-(*N*,*N*-dimethylaminomethylene) cyclic ketones (1c–9c)

Compound	δ(^{17}O)[a]	δ(^{13}C)[b]	Compound	δ(^{17}O)[c]	δ(^{13}C)[b]	Compound	δ(^{17}O)[a]	δ(^{13}C)[a]
1a	542.4	220.7	**1b**	502.5	208.4	**1c**	410.3	205.5
2a	555.3	212.2	**2b**	529.5	202.1	**2c**	432.2	197.9
3a	562.7	215.4	**3b**	530.4	204.8	**3c**	446.7	203.8
4a	563.7	218.5	**4b**	537.6	207.6	**4c**	442.8	203.5
5a	552.4	210.7	**5b**	515.5	201.9	**5c**	432.3	198.1
6a	544.3	199.8	**6b**	503.8	188.8	**6c**	443.5	198.4
7a	529.5	202.1	**7b**	490.9[d]	190.4	**7c**	385.8	187.3
8a	503.0[e]	207.0	**8b**	459.1	194.3	**8c**	368.2[e]	192.4[e]
9a	524.6	198.4	**9b**	487.2	187.9	**9c**	396.4	186.1

[a] Data taken from Ref. 4 unless indicated otherwise.
[b] $CDCl_3$ solution (0.5 M) at 20 °C.
[c] Acetonitrile solution at 40 °C unless indicated otherwise; linewidths at half-height are 240–340 Hz (780 Hz for **7b**; 490 Hz for **8b** and 580 Hz for **9b**).
[d] Measurement at 70 °C.
[e] This work.

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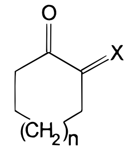
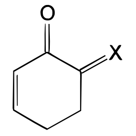


1 n = 0
2 n = 1
3 n = 2
4 n = 3



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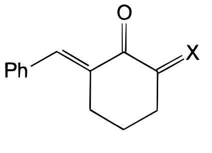

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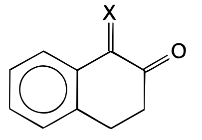

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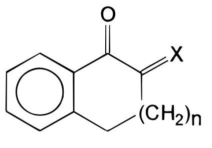

8 n = 0
9 n = 1

a: X = H_2 b: X = CHPh c: X = $CHNMe_2$

the carbonyl carbons of the three types of compounds (Table 1).

The ^{17}O chemical shifts of the 2-phenylmethylene cyclic ketones **1b**–**4b** are deshielded with increasing ring size and show same trend as those for the corresponding cyclic ketones (**1a**–**4a**) and 2-(*N*,*N*-dimethylaminomethylene) cyclic ketones (enaminones **1c**–**4c**).[4]

A benzene ring fused to 2-phenylmethylene cyclic ketone systems causes a shielding of the carbonyl O atom. Shieldings of 14 and 42 ppm were observed for **5b** and **9b**, respectively, compared with **2b**. This is attributed to extended conjugation of the carbonyl group with the unsaturated system. The effect of fusion of the benzene ring to the α,β-unsaturated system is an increase in shielding of 20–50 ppm per additional fused benzene ring, as noted previously for cyclohex-2-enone, α-tetralone and anthrone series and polycyclic quinone systems,[5] and has been explained in terms of a combination of the effect of increased conjugation of the carbonyl group with the additional benzene ring and γ-interactions with the *peri* hydrogens.[5] The large shielding observed for **9b** indicates that cross-conjugation of the carbonyl group with an additional unsaturated system is more efficient. The same effect of greater shielding, *ca.* 40 ppm, is observed for **6b**–**8b** relative to the corresponding α,β-unsaturated ketones **6a**–**8a**. Similar shielding effects (*ca.* 12 ppm), caused by the additional unsaturated systems in these compounds (**6b**–**9b**), are also observed for the ^{13}C chemical shifts of the carbonyl carbons.

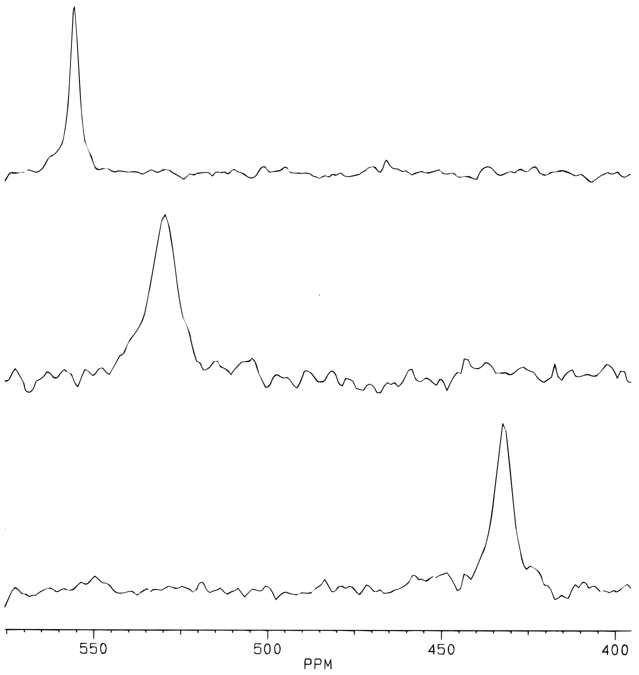

Figure 1. ^{17}O NMR (48.8 MHz) spectra of cyclohexanone (top, 0.5 M, 100 000 scans), 2-(phenylmethylene)cyclohexanone (middle, 0.5 M, 150 000 scans) and 2-(*N*,*N*-dimethylaminomethylene)-cyclohexanone (bottom, 0.5 M, 150 000 scans) in MeCN at 40 °C. Chemical shifts in ppm.

The ^{17}O and ^{13}C shift values of the respective C=O groups for the 2-phenylmethylene cyclic ketones **1b**–**9b** correlate well with those of the corresponding cyclic ketones (**1a**–**9a**) and with those of the corresponding 2-(*N*,*N*-dimethylaminomethylene) cyclic ketones (**1c**–**5c**, **7c**–**9c**) [Eqns (1)–(4)].

$$\delta(^{17}O)(\text{enone}) = 1.24\delta(^{17}O)(\text{ketone}) - 167.5 \qquad (N = 9,\ r = 0.987,\ \text{SD} = 4.4) \quad (1)$$

$$\delta(^{17}O)(\text{enone}) = 0.90\delta(^{17}O)(\text{enaminone}) + 132.0 \qquad (N = 8,\ r = 0.969,\ \text{SD} = 7.1) \quad (2)$$

$$\delta(^{13}C)(\text{enone}) = 1.00\delta(^{13}C)(\text{ketone}) - 10.0 \qquad (N = 9,\ r = 0.990,\ \text{SD} = 1.3) \quad (3)$$

$$\delta(^{13}C)(\text{enone}) = 1.03\delta(^{13}C)(\text{enaminone}) - 2.92 \qquad (N = 8,\ r = 0.989,\ \text{SD} = 1.3) \quad (4)$$

In Eqns (2) and (4), the point for **6b** was omitted owing to the deviation arising from its corresponding enaminone **6a**. These results demonstrate that cyclic effects in the three series are essentially identical, suggesting that common factors influence their ^{17}O and ^{13}C chemical shifts.

There are no acceptable correlation lines between the ^{17}O and ^{13}C chemical shifts of the respective C=O groups of the three types of compounds; in particular, the five-membered ring compounds **1a**–**c** and **9a**–**c** deviate owing to shielding of the O atom and deshielding of the C atom. The points for **6a**–**c** also deviate from the correlation lines. Omitting the points for **1**, **6** and **9**, the remaining points yield acceptable correlations [Eqns (5)–(7)].

$$\delta(^{17}O)(\text{ketone}) = 2.1\delta(^{13}C)(\text{ketone}) + 98.0 \qquad (N = 6,\ r = 0.989,\ \text{SD} = 2.7) \quad (5)$$

$$\delta(^{17}O)(\text{enone}) = 2.6\delta(^{13}C)(\text{enone}) - 6.7 \qquad (N = 6,\ r = 0.979,\ \text{SD} = 4.9) \quad (6)$$

$$\delta(^{17}O)(\text{enaminone}) = 3.2\delta(^{13}C)(\text{enaminone}) - 205.9 \qquad (N = 6,\ r = 0.977,\ \text{SD} = 6.0) \quad (7)$$

The 2-phenylmethylene cyclic ketones have been shown to exist in the *E*-form.[1] Previous IR and UV results have shown that either the carbonyl group or the benzene ring is twisted out of the plane of the C=C double bond in the enones.[6] X-ray crystallographic studies show that a dihedral angle between the C=O and C=C bonds of 6.5° is observed for **8b**[7] and 11.3° for **9b**.[8] ^{17}O NMR data for aryl ketones have been shown to correlate with torsion angles.[9] The relationship between the ^{17}O NMR data of the 2-phenylmethylene cyclic ketones **1b–9b** and those of the cyclic ketones **1a–9a** suggests that the changes on the dihedral angle between the C=O and C=C bonds for **1b–9b** are regular.

EXPERIMENTAL

^{17}O NMR spectra were recorded on a Bruker WH-360 spectrometer, equipped with a 10 mm probe, at 48.8 MHz, in the Fourier transform (FT) mode without lock. System control, data acquisitions and data management were performed by an Aspect-2000 microcomputer. The instrumental settings were spectral width 50 000 Hz (1025 ppm), 2K data points, pulse width 33 μs, acquisition time 20 ms, preacquisition delay 5 μs, 100 000–500 000 scans and sample spinning at 28 Hz. An even number (12–28) of left shifts (LS) were applied to FID signal; the latter was zero-filled to 8K words and exponentially multiplied with a 100 Hz line broadening factor (LB) before being subjected to FT. The chemical shifts δ_O, measured in 0.5 M acetonitrile solution at natural isotopic abundance, are reported relative to $\delta(H_2O) = 0.0$ ppm; dioxane ($\delta = 0$ ppm) was used as an external standard; downfield shifts are positive. The general reproducibility of chemical shifts values is within ±1 ppm.

Compounds

Compounds **1b–4b**,[10] **5b**,[11] **6b**,[12] **7b**,[13] **8b**[14] and **9b**[15] were prepared by literature procedures and characterized by their melting points and ^{1}H and ^{13}C NMR spectra.

Acknowledgements

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