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^{17}O NMR Spectra of α,β-Unsaturated Carbonyl Compounds RCH=CHCOX: the Influence of Group X on the $\delta(^{17}$O) Value of the Carbonyl Oxygen and on the Shielding Effect of Group R

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Abstract: ^{17}O NMR spectra of RCOX (R = Me, Ph), RCH=CHCOX (R = H, Ph, Me, CO_2Et) and Me_2C=CHCOX (X = H, Me, Et, i-Pr, t-Bu, Ph, PhCH=CH, OMe, OEt, Cl, CN, CF_3, CO_2Et) are reported. The ^{17}O shift values of these carbonyl compounds depend mainly on the electron donating power of X and correlate well with the resonance constants σ_R^+ of X. This suggests that the $\delta(^{17}$O) values can be used to reflect qualitatively the electrophilicity of the carbonyl group. The shielding effect of the substituent R in RCH=CHCOX is diminished with increasing the electronic donating power of X and correlates with σ^+ values of X.

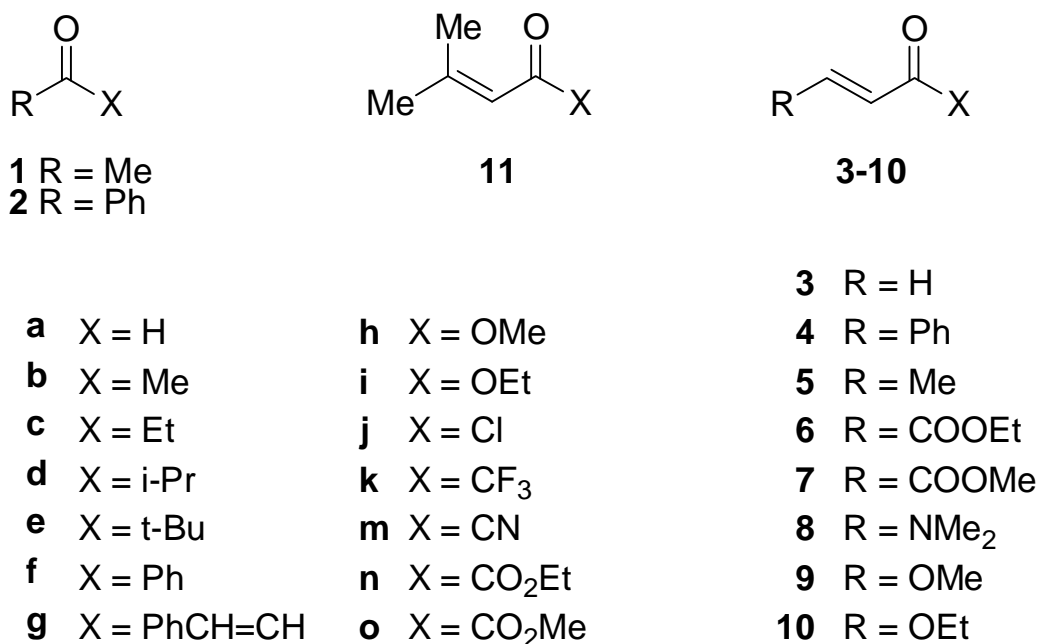**Keywords:** ^{17}O NMR; carbonyl groups; α,β-unsaturated carbonyl compounds; resonance effects.

Introduction

^{17}O NMR spectroscopy is a particularly useful tool for investigating the electronic state of carbonyl groups, including their electrophilicity [1, 2]. In RCOX derivatives, the shielding of O atom is increased with increasing the donating power of X group [2]. It has been shown by Dahn that the activity of the electrophilic carbonyl group, diminished by electron donating groups X, can be qualitatively reflected by the ^{17}O chemical shift values of the carbonyl oxygen [2].

Several types of α,β-unsaturated carbonyl compounds, as aldehydes, ketones and carboxylic acid

derivatives, are important organic derivatives [3, 4]. They have been extensively studied and have found a broad application in synthesis [3, 4]. ^{1}H and ^{13}C NMR spectroscopic studies have been applied to these compounds [3a, 5]. The [17]O spectra of a few α,β-unsaturated carbonyl compounds have been reported previously [1, 6], but they have so far not been systematically investigated. This paper describes a study of the influences of substituents X in RCH=CHCOX (Scheme 1) on the δ([17]O) value of the carbonyl O atom and on the shielding effect of group R.

![structure](O double bond, R–C(=O)–X)	–X)	–X)
1 R = Me	**11**	**3-10**
2 R = Ph		

3 R = H
4 R = Ph
5 R = Me
6 R = COOEt
7 R = COOMe
8 R = NMe$_2$
9 R = OMe
10 R = OEt

a X = H   **h** X = OMe
b X = Me   **i** X = OEt
c X = Et   **j** X = Cl
d X = i-Pr   **k** X = CF$_3$
e X = t-Bu   **m** X = CN
f X = Ph   **n** X = CO$_2$Et
g X = PhCH=CH   **o** X = CO$_2$Me

Scheme 1.

Results and Discussion

Effects of the X groups

The ^{17}O NMR data for a series of α,β-unsaturated carbonyl compounds (**3-11**) together with the data of the corresponding methyl and phenyl carbonyl compounds (**1** and **2**, respectively), obtained in acetonitrile solution at natural abundance, are summarized in Table 1 and Table 2. The ^{17}O NMR spectra of **3a**, **3b**, **3c**, **4f**, **4h**, **5a**, **5b**, **11b** and most of **1** and **2** have been already reported in various of solvents [1, 2]. In order to estimate difference substituent chemical shifts, these compounds were also measured under the same experimental conditions used here for α,β-unsaturated carbonyl compounds. The differences between literature data and the present values may arise from the solvent effects, temperature effects and external reference systems ($\delta_{ref.}$ = 0 ppm).

Table 1. ^{17}O NMR chemical shifts of **1-4** (solvent MeCN at 40°C)[a].

X	MeCOX		PhCOX		CH$_2$=CHCOX		PhCH=CHCOX		Δδ[b]
H	**1a**	596.6	**2a**	561.4	**3a**	584.1	**4a**	572.8	11.3
Me	**1b**	568.8	**2b**	548.4	**3b**	562.6	**4b**	554.3	8.3
Et	**1c**	556.4	**2c**	537.2	**3c**	545.7	**4c**	535.6	10.1
i-Pr	**1d**	553.6	**2d**	532.5	**3d**	533.3	**4d**	523.8	9.5
t-Bu	**1e**	556.6	**2e**	563.2[c]	**3e**	522.1	**4e**	514.5	7.6
Ph	**1f**	548.4	**2f**	549.6	**3f**	523.4	**4f**	513.7	9.7
PhCH=CH	**1g**	554.3	**2g**	513.7	-	-	**4g**	505.0	-
OMe[d]	**1h**	359.0	**2h**	337.5	**3h**	339.2	**4h**	335.9	3.3
OEt[e]	**1i**	358.5	**2i**	337.0	**3i**	338.1	**4i**	335.5	2.6
Cl	**1j**	504.4	**2j**	483.4	**3j**	492.7	**4j**	478.9	13.8
CF$_3$	**1k**	573.8	**2k**	543.6[f]	-	-	**4k**	561.5	-
CN	**1m**	603.4	**2m**	557.9	**3m**	583.6	**4m**	564.9	18.7
CO$_2$Et[g]	**1n**	582.9	**2n**	538.2[f]	**3n**	553.9	**4n**	538.9	14.7

a) Line-width (in Hz) at half-height: **1a-n** 40-240, **2a-n** 80-270, **3a-n** 40-190, **4a-n** 120-540 except for **4g** 730; b) Δδ = δ (**4**) - δ (**3**); c) Taken from Ref. 7; d) δ(OMe) for **1h**: 140.1, **2h**: 127.3, **3h**: 133.4, **4h**: 133.2 ppm; e) δ(OEt) for **1i**: 170.9, **2i**: 157.4, **3i**: 163.2, **4i**: 164.8 ppm; f) Taken from Ref. 2a. g) COOEt: δ(CO) for **1n**: 345.4, **3n**: 350.2, **4n**: 349.5 ppm; δ(OEt) for **1n**: 161.2, **3n**: 164.3, **4n**: 170.1 ppm.

Table 2. ^{17}O NMR chemical shifts of **5-11** (solvent MeCN at 40°C)[a].

X	MeCH=CHCOX		RO$_2$CH=CHCOX[b]		Me$_2$NCH=CHCOX[c]		ROCH=CHCOX[b]		Me$_2$C=CHCOX	
H	**5a**	564.6	-	-	**8a**	459.7	-	-	-	-
Me	**5b**	549.1	-	-	**8b**	455.7	**9b**[d]	521.7	**11b**	547.3
OEt	**5i**[e]	333.3	**6i**[f]	351.6	**8i**	295.2	-	-	**11h**[g]	342.6
Cl	**5j**	476.6	**6j**[h]	511.9	-	-	-	-	-	-
CN	**5m**	562.4	**6m**[i]	608.3	-	-	-	-	**11m**	554.7
CO$_2$R	**5n**[j]	536.6	**7o**[k]	579.3	**8n**	404.7	**10n**[l]	499.0	**11o**[m]	541.5

a) Line-width (in Hz) at half-height: 50-310; b) R = Et unless indicated otherwise; c) Taken from Ref 9; d) R = Me, δ(OMe) = 75.2 ppm; e) δ(OEt) = 161.9 ppm; f) δ(OEt) = 168.3 ppm; g) Compound **11h**: Me$_2$C=CHCOX, δ(OMe) = 168.3 ppm; h) COOEt: δ(CO) = 357.4 ppm; δ(OEt) = 171.1 ppm; i) COOEt: δ(CO) = 359.5 ppm; δ(OEt) = 171.9 ppm; j) COOEt: δ(CO) = 350.2 ppm: δ(OEt) = 164.7 ppm; k) R = Me. 1- and 2-COOMe: δ(CO) = 354.2 and 351.3 ppm; δ(OMe) = 140.0 and 134.6 ppm; l) R = OEt, δ(3-OEt) = 121.7 ppm; COOEt: δ(CO) = 347.1 ppm, δ(OEt) = 164.1 ppm; m) R = Me: δ(CO) = 344.4 ppm; δ(OMe) = 132.0 ppm.

The [17]O signals of the O atoms of α,β-unsaturated carbonyl compounds generally appear at higher field (6-50 ppm) than those of the corresponding methyl carbonyl compounds (**1**). The shielding effects for α,β-unsaturated carbonyl compounds have been previously reported in comparison with their saturated analogs and can be attributed to the conjugation of the carbonyl group with C=C double bond [1, 8].

The shielding of the carbonyl O atoms in the vinyl and styryl alkyl ketones (**3a**-**3e** and **4a**-**4e**, respectively) are enhanced with increasing volume of the substituent attached to the carbonyl group. The shielding trends are in the same direction as noted for those of the corresponding methyl ketones (**1a**-**1e**) and tertiary enaminones (**8a**-**8e**) [9]. The ^{17}O NMR data for the styryl ketones give a comparable correlation with those for the corresponding substituted enaminones [Eqs. (1) and (2)].

$$\delta_O(\mathbf{3}) = 1.48\ \delta_O(\mathbf{8}) - 103.0 \quad (n = 5, r = 0.966, SD = 7.5) \tag{1}$$

$$\delta_O(\mathbf{4}) = 1.43\ \delta_O(\mathbf{8}) - 92.2 \quad (n = 5, r = 0.974, SD = 6.2) \tag{2}$$

In the more extented conjugation systems (**4f** and **4g**), the [17]O signals of the carbonyls are considerably shielded to the upfield. A shielding of -40.6 ppm for **4f** and of -49.3 ppm for **4g** was observed in relative to **4b**. The shielding effects are consistent with the reduction of the double bond character of the carbonyl groups as a result of increased cross-conjugation with additional benzene ring or C=C double bond. The slight small shielding for phenyl substituent in **4f** can be ascribed to the twisting of the carbonyl group out of the plane of the C=C bond, a torsion angle of 16.9° for **4f** was noted previously by X-ray [10].

Introduction of an electron withdrawing group attached to the carbonyl group causes deshielding of the O atom. For example, the [17]O signals of the carbonyl oxygens of **1k** (573.8 ppm) and **4k** (561.5 ppm) appear at lower field than those of **1b** and **4b** by 5.0 and 7.2 ppm, respectively. This is in agreement with the increased the double bond character of the carbonyl group produced by an electron withdrawing group. Surprisingly, a large shielding of -34.7 ppm was observed for 4-MeOC$_6$H$_4$CH=CHCOCF$_3$ relative to 4-MeOC$_6$H$_4$CH=CHCOMe (Table 3). The same effect of greater shielding (-67 ppm) has been previously observed for **8k** as compared with **8b** [9].

Table 3. ^{17}O NMR data of 4-YC$_6$H$_4$COX and 4-YC$_6$H$_4$CH=CHCOX (solvent MeCN, unless indicated otherwise, at 40°C)[a].

	4-YC$_6$H$_4$COX			4-YC$_6$H$_4$CH=CHCOX		
X	Y = H	Y = OMe	$\Delta\delta$[b]	Y = H	Y = OMe	$\Delta\delta$[b]
Me	548.4	533.2[c]	-15.2	554.3	546.8[d]	-7.5
OMe	337.5[e]	330.5[f]	-7.0	335.9[g]	332.5[h]	-3.4
CF$_3$	554.0[i]	530.8[i]	-13.2	561.5	512.1[j]	-49.4

a) Line-width (in Hz) at half-height: 120-440; b) $\Delta\delta = \delta(\text{4-MeO}) - \delta(\text{H})$; c) $\delta(\text{4-OMe}) = 59.9$ ppm; d) $\delta(\text{4-OMe}) = 56.3$ ppm; e) $\delta(\text{OMe}) = 127.3$ ppm; f) $\delta(\text{OMe}) = 125.9$ ppm; $\delta(\text{4-OMe}) = 57.5$ ppm; g) $\delta(\text{OMe}) = 133.2$ ppm; h) $\delta(\text{OMe}) = 132.5$ ppm; $\delta(\text{4-OMe}) = 54.7$ ppm; i) Measurement in CCl$_4$, taken from Ref 2a; j) $\delta(\text{4-OMe}) = 63.0$ ppm.

For comparison, the ^{17}O spectra of several compounds $4\text{-}YC_6H_4COX$ and $4\text{-}YC_6H_4CH=CHCOX$ (Y=H and MeO) are given in Table 3. The shielding effect of the 4-MeO group is defined as $\Delta\delta = \delta(4\text{-}MeO) - \delta(H)$. The $\Delta\delta$ value for $4\text{-}MeOC_6H_4COCF_3$ (-13.8 ppm) [2c] is close to that for $4\text{-}MeOC_6H_4COMe$ (-15.2 ppm). It has been descibed that a C=C double bond inserted between the 4-substituted phenyl and carbonyl group results in a reduction of the substituent effects by approximately 50% [11]. This is true for $4\text{-}MeOC_6H_4CH=CHCOX$ (X = Me and MeO). In contrast, the $\Delta\delta$ value for $4\text{-}MeOC_6H_4CH=CHCOCF_3$ (-49.4 ppm) is considerably increased instead of being reduced. The greater shielding observed for $4\text{-}MeOC_6H_4CH=CHCOCF_3$ is consistent with the reduction of the double bond character of the carbonyl group, suggesting the important contribution of the resonance structure **B** (Scheme 2). Accordingly, a deshielding of 6.7 ppm for the 4-MeO group in $4\text{-}MeOC_6H_4CH=CHCOCF_3$, as compared with **8b,** is in agreement with the corresponding increased double bond character between the 4-MeO oxygen and phenyl group, as shown in **B**.
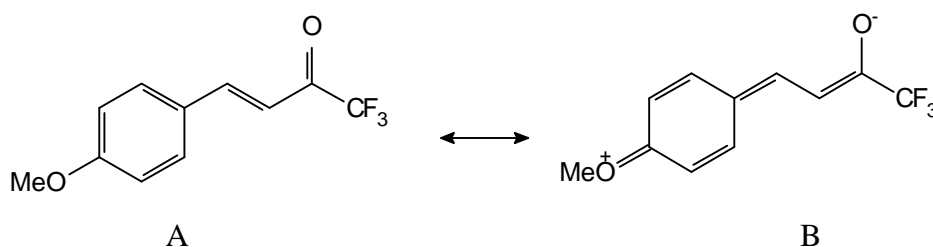
Scheme 2.

The CN group attached to the carbonyl group causes considerable deshielding of the carbonyl O atom, as compared with the corresponding Me derivative. The deshielding effect depends upon the structures and the number of β-substitutents. The deshielding is 34.6 ppm for acetyl cyanide (**1m**), as compared with **1b**. In the enhanced conjugation systems **2m** and **4m**, the deshielding effect of the CN group is reduced: 9.5 ppm for **2m** and 10.6 ppm for **4m** as compared with **2b** and **4b**, respectively. The deshielding was diminished by increasing the number of methyl groups at β-position of acroloyl cyanide (**3m**), ca. 7 ppm per methyl group: 21.0 ppm for **3m**, 13.3 ppm for **5m** and 7.4 ppm for **11m** in relation to **3b**, **5b** and **11b**, respectively. The diminished deshielding effects of the CN group in α,β-unsaturated system may attributed to the competition between the deshielding contribution arising from the inductive effects of the CN group and the shielding contribution arising from the cross-conjugation of the carbonyl group with CN group. The consequence of the latter effect would be expected to reduce the double bond character of the carbonyl group. The other reason for the observed deshielding of the CN derivatives compared with Me analogs is probably an effect due to the change of the energy of n-π* transition.

Similar results were observed for the $-COCO_2R$ derivatives **1n**, **2n**, **3n**, **4n**, **5n**, **10n** and **11o** (Tables 1 and 2) as shown by their ^{17}O data. A deshielding of 14.1 ppm is observed for ethyl pyruvate (**1n**) relative to acetone (**1b**); whereas the shielding (-5.8 to -22.7 ppm) is observed for **2n**-**10n** and **11o**

relative to the corresponding -COMe derivatives **2b**-**10b** and **11b**. The large shielding effect indicates an enhanced interaction of the substituent with the electron withdrawing CO_2R. The greater shielding of -51 ppm previously observed for **8n** (404.7 ppm) as compared with **8b** (455.7 ppm) has been explained in terms of the extended bond polarization and the increased n,π-conjugation in the N-C=C-C=O system [9].

In esters (**3h**, **3i**, **4h**, **4i**, **5i** and **6i**) and chlorides (**3j**, **4j**, **5j** and **6j**), as previously noted for saturated analogs [1], the increase in shielding of the O atom is attributed to the decrease in the π-bond order of C=O, explained by the resonance of the lone pair of electrons on O or Cl atom with the π-bond of the C=O group. The smaller shielding for the chlorides results from the interaction of the Cl atom with the C=O group is weaker, as compared with the ester derivatives.

The ^{17}O chemical shifts of MeCOX (**1**), PhCOX (**2**) and α,β-unsaturated compounds RCH=CHCOX (**3**-**6**) show that the shielding of the O atoms has the same trend and is enhanced with increasing the electron donating power of the X group. Good correlations are found between the $\delta(^{17}O)$ values of **2**-**6** and those of **1** [Eqs. (3) and (7)], indicating that the factors which affect the shielding of the O atom in **2**-**6** are parallel to those in **1**. The near-unity values of the slope of the correlation lines suggest that the steric and electronic effects of the substituents X on $\delta(^{17}O)$ values are essentially similar in MeCOX (**1**), PhCOX (**2**) and RCH=CHCOX (**3**-**6**).

$$\delta(^{17}O)(\mathbf{2}) = 0.96\ \delta(^{17}O)(\mathbf{1}) - 0.9 \quad (n = 13,\ r = 0.981,\ SD = 16.0) \tag{3}$$

$$\delta(^{17}O)(\mathbf{3}) = 1.00\ \delta(^{17}O)(\mathbf{1}) - 20.4 \quad (n = 11,\ r = 0.995,\ SD = 8.9) \tag{4}$$

$$\delta(^{17}O)(\mathbf{4}) = 0.97\ \delta(^{17}O)(\mathbf{1}) - 10.8 \quad (n = 13,\ r = 0.990,\ SD = 11.7) \tag{5}$$

$$\delta(^{17}O)(\mathbf{5}) = 0.95\ \delta(^{17}O)(\mathbf{1}) - 5.0 \quad (n = 6,\ r = 0.995,\ SD = 9.9) \tag{6}$$

$$\delta(^{17}O)(\mathbf{6}) = 1.03\ \delta(^{17}O)(\mathbf{1}) - 16.1 \quad (n = 4,\ r = 0.999,\ SD = 7.1) \tag{7}$$

(point for **7o** was included)

Resonance constants σ_R°, σ_R, σ_R^{-} and σ_R^{+} are considered to represent the resonance donor capacity of X [12]. The best correlations of the ^{17}O shift values of the carbonyl O atoms of **1**-**6** are with σ_R^{+} constants of X [Eqs. (8) and (13)]. There are no acceptable correlations between the ^{17}O shift values of **1**-**6** and σ⁺ constants [12] of X. These results demonstrate that the contribution of resonance structure **D** [R-CO-X (**C**) ↔ R-C(O⁻)=X⁺ (**D**)] in various carbonyl compounds RCOX is very important in the ground state of the molecules; the donor power of X plays a decisive role in determining the $\delta(^{17}O)$ values of the carbonyl -COX group and in their electrophilicities.

$$\delta(^{17}O)(\mathbf{1}) = 200.4\ \sigma_R^{+} + 599.7 \quad (n = 12,\ r = 0.979,\ SD = 17.7) \tag{8}$$

$$\delta(^{17}O)(\mathbf{2}) = 188.4\ \sigma_R^{+} + 572.8 \quad (n = 12,\ r = 0.941,\ SD = 29.1) \tag{9}$$

$$\delta(^{17}O)(\mathbf{3}) = 193.9\ \sigma_R^{+} + 569.7 \quad (n = 12,\ r = 0.968,\ SD = 21.5) \tag{10}$$

$$\delta(^{17}O)(\mathbf{4}) = 204.9\ \sigma_R^{+} + 584.6 \quad (n = 12,\ r = 0.972,\ SD = 21.8) \tag{11}$$

$$\delta(^{17}O)(\mathbf{5}) = 185.6\ \sigma_R^{+} + 561.6 \quad (n = 6,\ r = 0.956,\ SD = 29.2) \tag{12}$$

$$\delta(^{17}O)(\mathbf{6}) = 201.8\ \sigma_R^{+} + 592.0 \quad (n = 4,\ r = 0.984,\ SD = 24.8) \tag{13}$$

(point for **7o** was included)

*Effects of the **b**-substituent R in RCH=CHCOX*

The influence of the β-substituent R in RCH=CHCOX is clearly reflected by the [17]O shift value: an electron donating group (R = Me, OR, NMe$_2$) causes shielding; whereas an electron withdrawing causes deshielding (R = CO$_2$Me, CO$_2$Et). The shielding of the β-phenyl group (R = Ph, Table 1) in various α,β-unsaturated systems (**4a** - **4n**), as compared with those having the corresponding β-unsubstituted analogs (**3a** - **3n**), can be explained as resulting from the extended conjugation of the C=C-C=O system with the benzene ring. The shielding effect of the β-substituent R, i.e. the chemical shift difference between RCH=CHCOX and the corresponding CH$_2$=CHCOX: $\Delta\delta = \delta(^{17}O)_R - \delta(^{17}O)_H$, depends on a function of the substituent X attached to the carbonyl carbon. In β-phenyl series (**4**), the $\Delta\delta$ value for the electron-withdrawing CN group (**4m**) is -19 ppm, whereas for the electron donor EtO group (**4i**) is only -3 ppm. The negative value of the $\Delta\delta$ is increased in the order EtO < Me < H < Cl < CO$_2$Et < CN. The best correlation of the $\Delta\delta$ values is with σ^+ constants [12] of the corresponding X ($\Delta\delta$ = -11.5 - 10.3 σ^+, N = 11, r = 0.982, SD = 0.9). The shielding direction of a β-methyl group (R = Me) in various compounds MeCH=CHCOX is similar to that of the β-phenyl group, and shows slightly more sensitive to X.

It has been shown by Dahn that the resonance effects of electron donating geminal groups X in p-YC$_6$H$_4$COX are particularly important [2a,c]. The shielding of the O atom is increased and the sensitivity of the Y substituent is diminished with an increase in the donating power of the X groups. The present results are consistent with this conclusion.

Experimental

Materials

Compounds **3d**-**3f** [13], **3m** [14], **4m** [14], **5m** [14], **6m** [14], **3n** [15], **4c**-**4e** [16], **4g** [16], **4n** [17], **4k** [18], **5n** [19], **7o** [20], **11o** [21], 4-(4-methoxyphenyl)-but-3-en-2-one [22] and 4-(4-methoxyphenyl)-1,1,1-triflorobut-3-en-2-one [23] were prepared by literature procedures. The remaining coumpounds were commercially available (Fluka AG).

^{17}O NMR Spectroscopy

The ^{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 managements were performed by an Aspect-2000 microcomputer. Instrumental settings: spectral width 50 000 Hz (1025 ppm), 2 K data points, pulse width 33 μs, acquisition time 20 ms, preacquisition delay 5 μs, 200 000 - 500 000 scans, sample spinning (28 Hz). An even number (12-28) left-shifts (LS) were applied to FID signal; the latter was zero-filled to 8 K words and exponentially multiplied with 100-Hz line-broadening factor (LB) before being subjected to the FT. The

chemical shifts δ_o, measured in 0.5 M acetonitrile solution at 40°C at natural isotopic abundance, are reported relative to $\delta_o(H_2O)$ (=0.0 ppm); dioxane (δ_o = 0 ppm) was used as an external standard; downfield shifts are positive. The general reproducibility of chemical shifts values is ca. $\pm$ 1 ppm ($\pm$ 0.2 ppm within the same series).

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