^{13}C NMR Spectroscopic Study of the Tautomeric Equilibrium in *p*-Phenyl Substituted Benzoylacetones

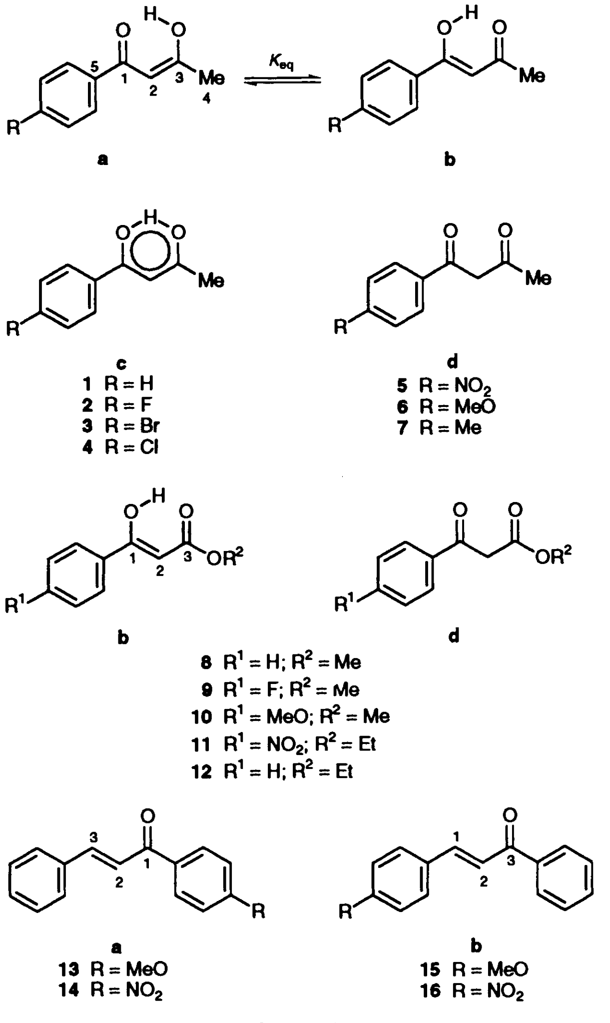
Raquel M. Cravero,[a] Manuel González-Sierra[a] and Alejandro C. Olivieri[b]
[a] *IQUIOS Facultad de Ciencias Bioquimicas y Farmaceuticas, Suipacha 531, Rosario (2000), Argentina*
[b] *Departamento de Quimica Analitica, Facultad de Ciencias Bioquimicas y Farmaceuticas, Suipacha 531, Rosario (2000), Argentina*

Solution ^{13}C NMR chemical shifts are reported for a series of *p*-phenyl substituted benzoylacetones which undergo a fast, intramolecular proton-transfer reaction between both possible enol tautomers. This information, together with ^{13}C NMR spectroscopic data for related non-exchanging model compounds, allows the study of substituent-induced equilibrium shifts. The results show a systematic trend: electron-withdrawing *para* groups shift the equilibrium towards the methyl keto form.

The chemistry of enols has traditionally attracted a great deal of attention.[1,2] Particular interest has been focused on the enolic forms of 1,3-diketones due to the tautomeric proton transfer equilibration in solution between two possible enol forms (Scheme 1). Both NMR and IR spectroscopic methods have been applied to the study of this equilibrium.[3-10] Several derivatives of acetylacetone,[11] benzoylacetone[12,13] and dibenzoylmethane[14,15] have also been studied in crystals by X-ray or neutron diffraction. Current interest in these compounds arises due to the suggested possibility of fast proton transfer in the solid state across the intramolecular hydrogen bond.[16,17]

Previous solution NMR spectroscopic work has characterized the enol forms mainly by means of ^{1}H chemical shifts.[7,8] Noteworthy features are the appearance of a highly deshielded, broad signal due to the labile OH hydrogen at *ca.* 16 ppm and a resonance at *ca.* 6 ppm ascribed to 2-H. ^{13}C[3,9] and ^{17}O[10] NMR spectroscopic data for simple 1,3-diketones have also been reported, and their use in the monitoring of tautomeric composition has been noted, although in some cases ^{13}C data have been interpreted on the basis of a resonance skeleton of type **c**[9] (Scheme 1). Information on the changes brought about by substituents in the equilibrium between tautomers **a** and **b** has also been gathered from crystal structure analyses of a series of dibenzoylmethane derivatives, on the assumption that crystals are built up from the predominant tautomer in solution.[15] However, recent careful X-ray structure determinations of benzoylacetone at very low temperatures have been shown to be consistent with the presence of a rapid solid-state $\mathbf{a} \rightleftharpoons \mathbf{b}$ equilibrium.[13,18]

It was therefore of interest to carry out a study on equilibrium constants in solution for a series of benzoylacetones with systematic substituent effects. Here we report ^{13}C NMR chemical shifts in $CDCl_3$ solution for compounds **2**–**7** in which the *p*-phenyl substituents have been selected so as to cover the range from strongly electron-donating to electron-withdrawing groups. Substituents may, in principle, have two kinds of influence on the carbon chemical shifts studied: one arising from changes in the enolic equilibrium composition, and an intrinsic substituent chemical shift (SCS) effect. Therefore, related model compounds were studied where the possibility of tautomerism is absent, in order to attempt a separation of the two effects mentioned above: enol esters **8**–**11** whose ^{13}C chemical shifts are reported herein, and chalcones taken from the literature (see Scheme 1 for structures and carbon numbering, which has been selected in order to maintain the same numbers for related carbons throughout the series).[19] After consideration of approximate intrinsic SCS effects, equilibrium constants are estimated for compounds **5** and **6**. In comparison with the parent compound **1**, the results suggest that the equilibrium $\mathbf{a} \rightleftharpoons \mathbf{b}$ is slightly shifted towards the methyl keto structure **b** when the electron-withdrawing ability of R increases and *vice versa*. Low temperature NMR spectroscopic data for compound **3** are also reported, revealing changes in ^{13}C chemical shifts which are consistent with a fast equilibrium between both enol tautomers, and are similar to those previously reported for the parent compound **1**.[17]



Scheme 1

Table 1 Solution ($CDCl_3$) 50 MHz ^{13}C chemical shifts (ppm) for compounds **1–7**

	Carbon							
Compound	1	2	3	4	5	6	7	8
1	183.15	96.53	193.64	25.63	134.67	128.44	126.83	132.13
2[a]	182.72	96.13	192.56	25.15	131.12	129.20	115.44	165.10
3	181.98	96.41	193.66	25.54	133.62	131.67	128.32	126.92
4	182.00	96.32	193.41	25.40	133.15	128.61[b]	128.12[b]	138.24
5	179.03	97.91	196.04	26.87	141.26	129.19	123.83	149.67
6	183.98	95.61	191.42	25.08	127.49	128.98	113.78	162.99
7	183.59	96.14	192.92	25.40	132.00	129.19	126.93	142.89

[a] Phenyl carbon shifts are averages of ^{13}C, ^{19}F *J*-doublets. [b] Assignments may be interchanged.

Experimental

Compounds **2–4**, **6** and **7** were prepared according to the following general procedure.[20] A mixture of ethanol (1 cm^3) and sodium (4.2 mmol) was heated at reflux under N_2 in a two-necked flask fitted with a sealed stirrer, a reflux condenser and a dropping funnel. After cooling with ice, dry ethyl acetate (1.7 cm^3) and the corresponding *p*-R-acetophenone (4.2 mmol) were added, causing the separation of the sodium salt of the *p*-R-benzoylacetone. The reaction mixture was stirred for 2 h and allowed to stand overnight. The solid was then dissolved in cold water, acidified with acetic acid, filtered and recrystallized from acetone–ethanol.

Compound **5**, on the other hand, was prepared by acid-catalysed condensation.[21] A mixture of *p*-NO_2-acetophenone (3 mmol) and acetic anhydride (12.1 mmol) was added to acetic acid–BF_3 complex (9.1 mmol) under ice cooling, stirred for 30 min, allowed to stand for 24 h at room temp. and poured into a solution of sodium acetate. The mixture was heated at reflux for 1 h, chilled and extracted with ether. The diketone was isolated by column chromatography.

Enol esters **8–10** were synthesized by base-catalysed (NaH) condensation of the substituted acetophenone with methyl carbonate.

Compound **11** was obtained from Aldrich.

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on a Bruker AC 200 spectrometer, operating at nominal frequencies of 200 MHz for ^1H and 50 MHz for ^{13}C. Chemical shifts were measured downfield from $(CH_3)_4Si$ used as an internal reference. Low temperature measurements were performed by cooling the driving gas with liquid nitrogen. Temperatures were measured with a previously calibrated thermocouple, and are considered accurate within ± 1 K.

AM1 calculations were performed by using the AMPAC package,[22] version 2.10, with gradient optimization on an IBM 3031 computer. In all cases the PRECISE option was used.

Results and Discussion

Satisfactory ^1H NMR spectra were obtained for diketones **1–7**, in all cases, signals corresponding to the labile enol proton were recorded at *ca.* 16 ppm, and those for 2-H at *ca.* 6.2 ppm. No signals that could be ascribed to the diketo form were detected. The ^{13}C NMR spectroscopic data are given in Table 1. Assignments were made by comparison with previously published data for **1**[3,16] and consideration of appropriate substituent chemical shift (SCS) increments[23] together with APT carbon spectra. In agreement with the ^1H NMR spectroscopic results, ^{13}C chemical shifts are interpreted as implying the existence of these compounds as a rapid **a** $\rightleftharpoons$ **b** equilibrium mixture, with no signals attributable to 1,3-diketo tautomers. In particular, carbon C-2 resonates in the range 96–98 ppm in all the compounds studied (Table 1), behaviour typical of the enolic forms **a**, **b**. Information on the position of the equilibrium between both tautomers can be gathered if suitable model compounds are selected in which tautomerism is absent. Carbonyl carbons in methyl vinyl ketone (δ_{CO} 196.1) and phenyl vinyl ketone (δ_{CO} 195.6) have been proposed as models for C-3 in **1b** and C-1 in **1a** respectively.[3] To account for the strong intramolecular hydrogen bond an extra shift of *ca.* 2 ppm should be added to these values.[3] We have taken 198 ppm as the extreme value both for the hydrogen bonded carbonyl carbon C-3 in **1b** and for C-1 in **1a**. On the other hand, the symmetric compounds dibenzoylmethane (δ_{CO} 186.0) and acetylacetone (δ_{CO} 192.5) provide chemical shifts for C-1 and C-3 which lie midway between the extremes.[3] This allows the estimation of values for C-3 in **1a** and C-1 in **1b** at about 187 and 174 ppm, respectively. On the other hand, since chemical shifts for carbon C-2 are 100.3 ppm in acetylacetone and 93.3 ppm in dibenzoylmethane, an average value of 96.5 ppm in **1** would be expected. Therefore, a shift in the **a** $\rightleftharpoons$ **b** equilibrium towards the methyl keto form **b** would induce an upfield shift in δ(C-1) and a corresponding downfield shift in δ(C-3), while δ(C-2) should be approximately independent of K_{eq}.

If the observed ^{13}C chemical shifts for carbons 1–3 in compounds **1–7** (Table 1) are qualitatively compared with those discussed above for tautomers **1a** and **1b**, it may be concluded that appreciable amounts of both enols exist in all the compounds studied, with form **b** being slightly preferred in all cases. A quantitative study can be carried out if, as is customary, the equilibrium constant for a given diketone is calculated from the most sensitive carbon chemical shift (C-1) by using the relation:

$$K_{eq} = (\delta_a - \delta)/(\delta - \delta_b) \qquad (1)$$

where δ is the experimental ^{13}C chemical shift assigned to C-1 and δ_a and δ_b are the corresponding values in tautomers **a** and **b**. The value so obtained[3] for K_{eq} in **1** (K_{eq} = 1.6) reasonably agrees with that previously calculated from ^{17}O NMR spectroscopic data (K_{eq} = 1.3).[10] Similar calculations could be performed for the other diketones studied, provided that information was available on the corresponding extreme resonances δ_a and δ_b for carbon C-1. Since the latter could be influenced by the nature of the substituent R, attention was focused on model compounds which do not show this kind of tautomeric equilibration, in order to gather information on the remote effect of the R groups on carbons 1–3. Table 2 shows the observed ^{13}C chemical shifts for compounds **8–12**. Esters **8–10** are present in $CDCl_3$ solution as an equilibrium between a single enol form **b** and the keto form **d** (Scheme 1). The equilibrium is slow on the NMR time-scale, since separate lines are observed for these forms both in the ^1H and ^{13}C spectra. Tautomers having structure **b** show characteristic ^1H NMR signals at 12.5 ppm (OH) and 5.6 ppm (2-H), whereas in those having structure **d**, 2-H appears at *ca.* 4.0 ppm. The ratio **b** : **d** can be easily computed from the relative areas for 2-H (Table 2). As expected,[24] the electron-withdrawing ability of R has an

Table 2 Solution ($CDCl_3$) 50 MHz ^{13}C chemical shifts (ppm) for compounds **8**–**11**, and calculated values for the ratio between **b** and **d** tautomers

Compound	Carbon 1	2	3	Ratio **b**:**d**[a]
8b	170.84	86.43	172.90	1:11
8d	191.92	44.93	167.40	
9b	173.13	86.50	170.05	1:7
9d	190.58	45.41	167.49	
10b	171.24	85.25	173.56	1:16
10d	190.69	45.41	168.05	
11b[b]	168.26	90.22	172.61	
12b[c]	171.5	87.4	173.3	

[a] Measured from the integrated signals of 2-H. [b] The assignment of carbons C-1 and C-3 was confirmed by observing the isotopic effect upon replacement of the OH hydrogen by deuterium; in agreement with other observations,[28] we obtained $^2\Delta$(C-1) = +0.36 ppm; $^4\Delta$(C-3) = +0.18 ppm. [c] Ref. 29.

Table 3 AM1 calculated excess π electron densities at carbons 1–3 in diketones **5** and **6**, enol esters **10b** and **11b** and chalcones **13**–**16**, and relevant AM1 distances for selected 1,3-diketones

	AM1 Calculated excess π electron densities[a] (× 10^4)		
Compound	C-1	C-2	C-3
6b	−34	+68	−1
10b	−39	+74	−3
15	−65	+131	−9
5b	+238	−289	+7
11b	+235	−326	+25
16	+298	−407	+71
6a	+6	−11	+20
13	+34	−11	+30
5a	+79	+164	−200
14	+26	+224	−225

	AM1 distances (Å)					
Distance	**1a**	**1b**	**5a**	**5b**	**6a**	**6b**
C-2–O	1.361	1.246	1.359	1.245	1.361	1.246
C-2–C-3	1.357	1.454	1.359	1.458	1.357	1.454
C-3–C-4	1.455	1.360	1.451	1.358	1.456	1.361
C-4–O	1.247	1.364	1.246	1.364	1.248	1.365
O···O[b]	2.808	2.815	2.816	2.804	2.805	2.805
O–H[c]	0.975	0.975	0.975	0.975	0.975	0.975
O···H[d]	2.025	2.022	2.035	2.015	2.023	2.012

[a] The excess is given with respect to the corresponding unsubstituted parent compound (see Scheme 1 for carbon numbering). [b] Distance between the enolic oxygens. [c] Distance between the enolic oxygen and its attached hydrogen. [d] Distance between the carbonylic oxygen and the labile hydrogen.

influence on the position of the equilibrium **b** $\rightleftharpoons$ **d**, favouring the enol ester **b**. Carbon chemical shifts are also indicative of the existence of a slow equilibrium **b** $\rightleftharpoons$ **d**, with signals arising from C-2 at *ca.* 85 ppm in the enol form **b** and 45 ppm in **d** (Table 2). Esters **11** and **12** appear to exist as only **b** tautomers (Table 2). Chemical shifts of CO carbons in the enolic form **b** suffer minor SCS effects, while the enolic carbon C-2 seems to be the most affected: $\Delta\delta_2(NO_2)$ + 2.87; $\Delta\delta_2$(OMe) −1.18 ($\Delta\delta_i$ is defined as the difference between the chemical shifts of carbon *i* in the substituted and parent compounds). These results are in agreement with those previously reported for a series of chalcones having the general structure **b** (see Scheme 1), in which the most affected carbon was also found to be C-2: $\Delta\delta_2(NO_2)$ +3.90; $\Delta\delta_2$(OMe) −2.27.[19] This was explained on the basis of MO calculated π electron densities at carbons 1–3.[19] Table 3 shows the AM1-calculated excess π electron densities at these carbons (relative to the unsubstituted parent compound) in several chalcones, as compared with the corresponding values in enol esters having the tautomeric structure **b**, as well as with 1,3-diketone tautomers **a** and **b**. It can be seen that the π electron density changes are comparable among all groups of compounds both in magnitude and sign. Further, the largest effect on structures of type **b** corresponds to carbon C-2, in agreement with the experimental data. The observed SCS effects for R = NO_2 ($\Delta\delta_1$ −3.2) and MeO ($\Delta\delta_1$ +0.40, see Table 1) at carbon C-1 in the enol esters **11b** and **10b** (with respect to **12b** and **8b** respectively) are also similar to those in the corresponding chalcones of type **b** (R = NO_2, $\Delta\delta_1$ −2.93; R = MeO, $\Delta\delta_1$ +0.07),[19] and hence they can be used to correct the extreme chemical shifts δ_b for the most sensitive carbon C-1 in benzoylacetone tautomer **1b**. We estimate values of δ_b at 170.8 ppm in **5b** (R = NO_2) and 174.4 ppm in **6b** (R = MeO). Corresponding values for δ_a are calculated from SCS effects on chalcones of type **a**: $\Delta\delta_1(NO_2)$ −1.14; $\Delta\delta_1$(OMe) −1.95,[19] leading to corrected values of 196.9 and 196.1 for carbon C-1 in **5a** and **6a**, respectively. Hence, application of eqn. (1) yields the following equilibrium constants: K_{eq} = 2.2 for R = NO_2 (diketone **5**) and 1.3 for R = OMe (diketone **6**). An analogous calculation for R = F gives a value for K_{eq} which is very similar to that for compound **1**, indicating that substituents with weak electronic demands may not have significant effects on the position of the equilibrium. On the other hand, the results for strongly influencing substituents show a systematic trend: equilibria are displaced (though very slightly) towards the methyl keto structure **b** when the electron-withdrawing properties of R increase, and *vice versa*. As discussed above, the chemical shift for carbon C-2 may be expected to be approximately independent of the value of K_{eq}, but may, however, be influenced by an intrinsic SCS effect. Since $\Delta\delta_2$ for NO_2 and MeO groups in chalcones of type **a** are −0.49 and −0.16 ppm, respectively,[19] considerably smaller than those expected for **b** forms (see above), the overall effect would be to deshield carbon C-2 on increasing the electron-withdrawing nature of R, as observed (Table 1).

Further characterization of the existence of an equilibrium **a** $\rightleftharpoons$ **b**, in the 1,3-diketones studied, which is displaced towards tautomer **b** is provided by variable temperature ^{13}C NMR spectroscopic measurements. Chemical shifts for carbons 1 and 3 in benzoylacetone[17] have been shown to be temperature-dependent, with the changes being interpreted as a result of a favouring of tautomer **1b** on cooling. In Table 4 the presently obtained results for compound **3** in $CDCl_3$ solution are collected. As can be seen, small changes are detected in carbons 1 and 3 on lowering the temperature. As expected from the above discussion, the changes are of opposite sign and suggest the existence of an approximately equimolecular equilibrium which is displaced towards **3b** on cooling. Furthermore, no appreciable changes are observed in carbon C-2, since in this case the observed effects are only due to changes in K_{eq}.

The information obtained is not only relevant concerning the structures of simple 1,3-diketones in solution but also on those occurring in the solid state. Crystal structures for compounds **1**,[12,13] **3**,[25] and **5**[26] have been reported, as well as for many derivatives of acetylacetone and dibenzoylmethane.[11–15] In general, diffraction results have been interpreted as implying the existence of static, resonant structures of type **c**, which are assumed to resemble the most populated tautomer present in solution. Consideration of several crystal structures (as regards C–O bond distances and position of the enol hydrogen) has led to the prediction that the labile proton prefers the site corresponding to the minimum electron density.[15] Although

Table 4 Variable-temperature 50 MHz ^{13}C chemical shifts (ppm) for compound **3**

T/K	Carbon C-1	C-2	C-3
297	181.98	96.41	193.66
287	181.93	96.41	193.82
277	181.85	96.41	193.93
267	181.78	96.41	194.01
257	181.71	96.40	194.07
247	181.65	96.40	194.14
237	181.57	96.40	194.24
227	181.53	96.39	194.26

this appears to agree both with previous solution NMR work on related 1,3-diketones and with the present results, several exceptions to this general rule were also observed. However, recent structure determinations of **1** at 20 K suggest that the dynamic equilibrium **a** $\rightleftharpoons$ **b** is also present in crystals of this compound,[13] leading to average values of C–O bond lengths (C-1–O, 1.299 and C-3–O, 1.293 Å).[13] It is conceivable, therefore, that other benzoylacetones could exist as similar tautomeric mixtures in the solid phase. The reported C–O distances in diketones **3** and **5** are C-1–O, 1.306 and 1.297 Å; C-3–O, 1.290 and 1.289 Å respectively.[25,26] These results could also be due to the existence in these crystals of rapid proton-transfer equilibria (although tautomer **b** seems to be the preferred one in both cases) leading to weighted averages for the C–O bond lengths. The observed averages lie midway between those expected for true C–O and C=O bonds (1.35 and 1.25 Å, respectively).[18] It should be noticed that solid-state values of K_{eq} can be influenced by several factors beyond those caused by substituents: intermolecular interactions (most notably hydrogen bonds) and changes in twisting angles between phenyl and enol rings.[16] These perturbations appear to be small enough so that the results obtained in solution are also generally obeyed in the solid state. Although the presently observed trend in solution appears to be free from such subtle complications which are peculiar to the solid phase, the question of finding an explanation for the observed substituent effects is however an interesting one. This is because the relation of the substituent group R and the subunits in the enol ring of tautomer **a** become the vinylogous ones in tautomer **b**. We have attempted to answer this question by using the semi-empirical MO program AM1, reputed as being able to optimize molecular structures where hydrogen bonding is involved.[27] Table 3 shows relevant AM1 parameters for selected enolic 1,3-diketones after performing a full geometry optimization. As previously discussed for **1**,[17] no energy minimum such as **c** is found by AM1. Rather, the latter seems to resemble the transition state for the proton-transfer reaction. Geometries obtained for tautomers **a** and **b** show the labile hydrogen as clearly bonded to one of the oxygen atoms, while alternation of bond lengths within the enol ring is also apparent. Calculated enthalpies of formation of the enolic forms **a** and **b** are very similar in all cases, with the differences being probably not significant at the level of accuracy of AM1: $\Delta(\Delta H_f^0)$ for **1**–**7** are 0.6, 0.8, 0.7, 0.8, 0.6, 0.4 and 1.0 kcal mol^{-1},* respectively. This agrees with the NMR spectroscopic data discussed above which showed that R groups are only able to induce very minor shifts in the equilibrium **a** $\rightleftharpoons$ **b** in the compounds studied.

In conclusion, it has been shown that the tautomeric equilibrium between the enol forms of *p*-R-benzoylacetones is slightly displaced towards the methyl keto form by electron-withdrawing substituents. Equilibrium constants have been estimated when R = OMe and NO_2 from the observed ^{13}C chemical shifts of carbon C-1 in $CDCl_3$ solution, together with the consideration of suitable model compounds. Variable temperature NMR spectroscopic measurements on the *p*-Br derivative confirms the existence of an equilibrium which is shifted towards the methyl keto structure on cooling. The application of the semi-empirical MO program AM1 concerning both molecular geometries and enthalpies of formation is also discussed. Implications regarding solid-state structures have also been drawn.

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* 1 cal = 4.184 J.

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