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OXYGEN-17 NMR STUDY ON SUBSTITUTED α,α,α-TRIFLUOROACETOPHENONES*

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ABSTRACT

An excellent linear correlation of oxygen-17 substituent chemical shifts (SCS) for twelve α, α, α-trifluoroacetophenones with single σ^+ constants, $\delta = 24{\cdot}6\sigma^+ + 556{\cdot}3$ (correlation coefficient 0·998) has been observed. However, from this plot, an SCS of 34·3 ppm for 1, 1, 1-trifluoroacetone will give a corresponding σ^+ (γ^+) value of 1·44 for a methyl group, which is not in agreement with 0·63–0·79 obtained from solvolytic rate data.

Measurements of oxygen-17 NMR chemical shifts have been successfully employed as a tool for the study of structural effects on acetophenones[1–5] and other series of aromatic compounds.[6] In cases where the electronic effects of *meta* and *para* substituents are concerned, correlations of substituent chemical shifts (SCS) with dual substituent parameters (DSP)[7] have generally been observed. It has been reported that the ^{17}O chemical shifts of substituted anisoles show a good linear correlation with σ^-.[8] On the other hand, in this study the first example of an excellent linear correlation of ^{17}O SCS values for α,α,α-trifluoroacetophenones (**1a**–**l**) with single σ^+ constants is realized.

The substituted α,α,α-trifluoroacetophenones **1a**–**e** and **1g**–**l** were synthesized from the corresponding aryl halides via a Grignard reaction with trifluoroacetic anhydride at −70 °C.[9] (The ketones **1a**, **1b** and **1d**–**j** showed IR and ^{19}F NMR spectra identical with the literature data.[9–11] For ketones **1c** and **1k**–**1l**, both the spectral and the analytical data (C, H) were in agreement with the assigned structures.) A 0·5 M solution of the ketone, **1** or 1, 1, 1-trifluoroacetone (**2**), in carbon tetrachloride was dried over 4A molecular sieve before it was transferred into an NMR tube for measurement (the drying is essential because the ketone form hydrates readily[12]). [The ^{17}O spectra were recorded on a Bruker AM-300WB spectrometer equipped with a 10-mm broad-band probe operating at 40·688 MHz. All chemical shifts were measured relative to an external deuterium oxide reference. The instrument settings were 50 kHz spectral width, 2K data points, 90° pulse angle (12·5 μs pulse width), 1 ms acquisition delay and 16 ms acquisition time. The signal-to-noise ratio was improved by

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Table 1. Oxygen-17 chemical shifts for trifluoroketones[a]

$ArCOCF_3$	Ar	σ^{+b}	$\delta_{(C=0)}$	$\delta_{(other)}$
1a	5′-Coumaranyl	$-0{\cdot}984^c$	531·0	99·1
1b	4′-$CH_3OC_6H_4$	$-0{\cdot}778$	537·1	62·4
1c	4′-$C_6H_5OC_6H_4$	$-0{\cdot}560^d$	543·2	114·4
1d	4′-$CH_3C_6C_4$	$-0{\cdot}311$	549·7	
1e	3′-$CH_3C_6H_4$	$-0{\cdot}066$	554·4	
1f	C_6H_5	0·000	557·6	
			$556{\cdot}5^e$	
1g	3′-FC_6H_4	0·352	563·8	
1h	3′-ClC_6H_4	0·399	564·7	
1i	3′-$CF_3C_6H_4$	0·520	568·5	
1j	4′-$CF_3C_6H_4$	0·612	572·6	
1k	3′,5′-$Cl_2C_6H_3$	$0{\cdot}701^f$	574·4	
1l	3′,5′-$(CF_3)_2C_6H_3$	$0{\cdot}946^g$	579·2	
2	CH_3		$591{\cdot}8^e$	

[a] Measured at 60 °C unless stated otherwise.
[b] From ref. 13 unless stated otherwise mentioned.
[c] Ref.15.
[d] Ref. 14.
[e] measured at 25 °C.
[f] Ref. 17.
[g] Ref. 16.

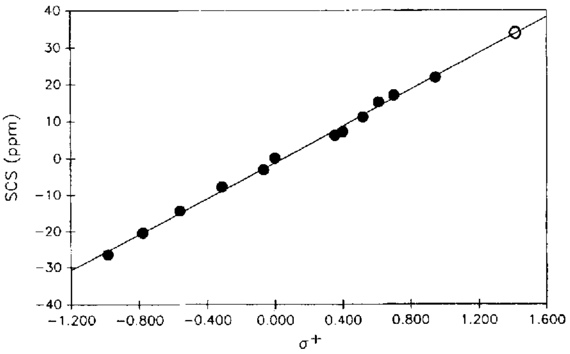
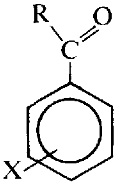


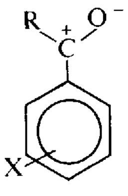
Figure 1. Plot of ^{17}O SCS in trifluoroacetophenones against σ^+

applying a 25 Hz exponential broadening factor to the free induction decay prior to Fourier transformation. Generally, spectra with a signal-to-noise ratio of ca 10:1 were obtained from 10^5–10^6 scans.] The observed ^{17}O chemical shifts at natural abundance are listed in Table 1. An excellent linear plot (Figure 1) was obtained from the correlation analysis of SCS for $\delta_{^{17}O}$ with a large range of σ^+ constants ($-0{\cdot}984$ to $0{\cdot}946$):[13–17] $\delta = 24{\cdot}6\sigma^+ + 556{\cdot}3$ (correlation coefficient 0·998).

The ^{17}O SCS values for acetophenones were found to have best fits with dual parameters, σ_I and σ_R^+: $\delta = 18{\cdot}6\sigma_I + 24{\cdot}0\ \sigma_R^+$[2] and $\delta = 20{\cdot}9\sigma_I + 21{\cdot}9\sigma_R^+$.[3] Less satisfactory correlations resulted from the use of the single-parameter method with σ ($r = 0{\cdot}92$) or with σ^+ ($r = 0{\cdot}96$).[2] Although a direct conjugation between the carbonyl oxygen and the aryl ring is unlikely, the $\delta_{^{17}O}$ in substituted acetophenones has been considered to be dependent on the relative contributions from the canonical structures **3a–e** (R = CH_3),[2] and has been found to correlate well with the π-electron densities obtained from *ab initio* MO calculations.[3] The present observation of the excellent linear relationship between ^{17}O SCS values with σ^+ constants for **1** is probably due to the presence of the strong electron-attracting trifluoromethyl group, which may increase the weight of contributions from the dipolar structures **3b–e** (R = CF_3) significantly.



3a



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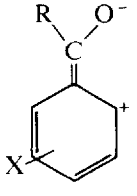
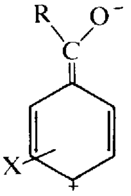
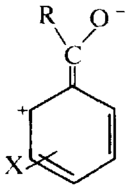


3c



3d



3e

It is also interesting that the downfield shift of the ^{17}O chemical shift for **2** is large compared with that for **1**. Moreover, from this plot an SCS of 34·3 ppm for **2** (open circle) will give a corresponding σ^+ (γ^+) value of 1·44 for the methyl group, which is not in agreement with the value of 0·63–0·79 obtained from the solvolytic rate data, assuming that it can be regarded as a deactivating aryl group.[18,19] Comparison of the rate of solvolysis for 1,1,1-trifluoro-2-phenyl-2-propyl tosylate vs that for the 2,2,2-trifluoro-1,1-diphenylethyl analogue in 80% ethanol[20] would yield a corresponding value of 0·81 for the methyl. Although both the solvolytic reactivities of various tertiary benzylic substrates with[20] or without[18] an α-trifluoromethyl group and the ^{17}O SCS values observed in the present study exhibit excellent Hammett–Brown plots with σ^+ constants, there is a significant difference between these two extrapolated γ^+ values for the methyl group (1·44 vs 0·63–0·79). This suggests that there might be little interrelation between the chemical shift of the aromatic acyl oxygen and the benzylic reactivities for solvolysis. Other spectroscopic studies on **1** are in progress.

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