Carbon-13 NMR Spectra of Some 4-**Substituted Phenacyl Bromides**

The ¹³C NMR signals for some 4substituted phenacyl bromides were assigned. The experimental chemical shifts of the aromatic ring carbons are in close agreement with those calculated using substituent chemical shifts. Both the carbonyl and the α -methylene carbons exhibit upfield shifts compared with those of the corresponding 4-substituted acetophenones.

INTRODUCTION

Although 4-substituted phenacyl bromides, XC₆H₄COCH₂Br, are important starting materials for several synthetic routes, there is a lack of NMR data for these compounds in the literature. The purpose of this work was to optimize their preparation conditions and to record their IR and ¹H and ¹³C NMR data for their full characterization.

RESULTS AND DISCUSSION

4-Substituted phenacyl bromides 1-4, 6 (Table 1) were prepared from the corresponding acetophenones by bromination in diethyl ether-dioxane solution.1 4-Methoxyacetophenone did not lead to the corresponding bromide (5) under these conditions, but required the addition of a mixture of bromine and aluminium trichloride in diethyl ether solution.² The physical constants of 1-6 agreed with the published data1 and their IR and 1H NMR data are included in Table 2.

The ¹³C NMR experimental and calculated chemical shifts are shown in Table 1. The signals of the aromatic carbons were assigned by single-frequency off-resonance decoupling (SFORD) and known chemical shift rules.³ The substituent chemical shifts were taken from Ewing's tabulation⁴ and, for the COCH₂Br group, estimated from the chemical shifts of the unsubstituted phenacyl bromide 1. The close agreement between the two data sets indicates the correctness of the assignments.

The calculated chemical shifts for the α methylene carbon deviate from the experimental values by more than 10 ppm [e.g. 1, δ (calc.) = -2.3+26.9+20.0 = 44.6; δ (exp.) = 32.0 ppm]. Non-additivity (NA) effects have been attributed5 to through-bond and through-space orbital interactions, which should be operative in the COCH2Br system.

The carbonyl carbon of 1-6 exhibits an upfield shift compared with the corresponding acetophenones, which may be due either to the inductive effect of the bromine atom⁶ or to the orbital interactions mentioned above.

Table 1. ¹³C chemical shifts^a of 4-substituted phenacyl bromides

Substituent	Compound	CH₂	C==0	C-1	C-2,6	C-3,5	C-4	Others
н	1	32.0	192.1	134.9	129.8	129.8	134.9	
Me	2	32.1	190.6	131.2	128.8	129.4	145.5	21.8
				131.8	129.7	130.5	144.1	
Cl	3	31.6	189.9	132.0	130.1	129.4	140.2	
				133.0	131.2	130.2	141.1	
Br	4	31.5	191.2	133.6	131.4	133.2	130.2	
				133.3	131.4	133.1	129.0	
OMe	5	31.9	190.8	127.8	132.3	115.0	165.0	56.6
				127.2	130.9	115.4	166.2	
NO ₂	6	31.4	190.8	139.4	131.0	125.0	151.6	
				141.0	130.7	124.9	154.7	

a In ppm relative to TMS. The second entries are those calculated using substituent chemical shifts.

Table 2. Physical and spectral data for the 4-substituted phenacyl bromides											
Compound	M.p. (°C)	$v_{\rm CO}({\rm cm}^{-1})^{\rm a}$	H-2,6 ^b	H-3,5	CH₂	Others					
1	51	1710	7.7	/ (m)°	4.46						
2	95–97	1709	7.4	8.0	4.47	2.41					
3	108-109	1710	7.6	7.8	4.40						
4	52	1705	7.3	7.8	4.40						
5	74-75	1700	6.9	7.8	4.40	3.92					
6	97–98	1716	8.2	8.3	4.50						

ª In CCl₄.

^b ¹H NMR chemical shifts, in ppm relative to TMS, for CDCl₃ solutions. ^c m = multiplet.

EXPERIMENTAL

Materials

The 4-substituted phenacyl bromides were prepared by literature procedures.^{1,2} The physical and spectral data are shown in Table 2.

Spectra

The ¹³C NMR spectra of 0.5 M solutions in CDCl₃ with 5% TMS as an internal reference, in 12 mm o.d. sample tubes, were recorded at 25.2 MHz using a Varian XL-100-15 spectometer in the FT mode. The conditions were as follows: deuterium internal lock; temperature ca. 31 °C; pulse width 10 μ s; flip angle 25°; acquisition time 0.8s; spectral width 5000 Hz; pulse repetition time, 1.7 s; number of transients, 6000; and number of data points, 8192. The ¹³C NMR spectra were recorded both in the protonnoise decoupled and in the single-frequency off-resonance decoupled modes.

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