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CARBON-13 NMR OF ALIPHATIC KETONES

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ABSTRACT

This work reports unpublished Carbon-13 NMR chemical shift data of three aliphatic ketones: 2-octanone, 2-nonanone and 2-undecanone; and corrected data for 2-hexanone (C-4) and 2-decanone (C-1; C-2). The empirical substituent effects of the CH_3CO group were determined more accurately and can be useful in correlation analysis.

RESUMO

Este trabalho relata dados não publicados e inéditos de deslocamentos químicos de RMN de Carbono-13 para três cetonas alifáticas: 2-octanona, 2-nonanona e 2-undecanona; e dados corrigidos da 2-hexanona (C-4) e 2-decanona (C-1; C-2). Os efeitos empíricos do substituinte do grupo CH_3CO foram determinados mais acuradamente e podem ser úteis em análise correlacional.

KEY WORDS: Carbon-13 NMR, chemical shift, aliphatic ketones.

INTRODUCTION

Recently we have studied aliphatic compounds by Carbon-13 NMR spectroscopy[1]. Although aliphatic ketones are important starting material for some syntetic routes, there is a lack of NMR data in the literature[2]. We have synthetized some aliphatic ketones like $\mathbf{CH_3COCH_2R}$ where **R** is an alkyl group containing one to eight carbon atoms (methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl and octyl). The purpose of this work was to sinthesize several non-branched aliphatic ketones with sp^3 hybridization, to record their Carbon-13 NMR data for their full caracterization, and to determine the empirical effects to the $\mathbf{CH_3CO}$ group. The Carbon-13 NMR chemical shifts data of three aliphatic ketones: 2-octanone, 2-nonanone and 2-undecanone have not been reported in the literature. The empirical substituent effects of the CH_3CO group were determined more accurately and can be useful in correlation analysis.

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EXPERIMENTAL PROCEDURE

Materials: All compounds were prepared by using ethyl acetoacetate synthesis: the β-keto esters alkylated by convenient alkyl halide followed by hydrolysis and decarboxylation to lead to aliphatic ketones like **CH_3COCH_2R** where **R** is an alkyl group containing one to eight carbon atoms (methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl and octyl), according to a procedure described in the literature[4]. The physical and spectral data are shown in Tables 1-3. Solventes were of spectroscopic quality and were used without further purification.

Spectra: The C-13 NMR spectra of 1,0 M solutions in $HCCl_3$ with 1% TMS as an internal reference in 10 mm o.d. sample tubes, were recorded at 25,2 MHz using a Varian XL 100 spectrometer in the FT mode. The conditions were as follow: pulse width, 20 μs; acquisition time, 0,67 s; spectral width, 6150 Hz; pulse repetition time, 0,4 s; temperature, 30 °C; internal lock, D_2O; angle tumbling, 45°; number of transients, 6000; and number of data point, 8192. The C-13 NMR spectra were recorded in both the single-frequency off-resonance decoupling and proton noise decoupled in the FT mode.

RESULTS AND DISCUSSION

Table 1 shows the physical constants obtained for these compounds. They agree with published data. The Carbon-13 NMR data are shown in Table 2. The signals of aliphatic carbons were assigned by known chemical rules[2]. The compound 2-hexanone was synthesized to correct the C-4 signal (δ = 31,9 according the literature[2]; we have found δ = 25,2). The compound 2-decanone was synthesized to correct the C-1 and C-2 signals (δ = 28,9 and 208,0 respectively), until now unavailable in the literature. All compounds were synthesized to complete the data set to define the empirical substituent effects of the CH_3CO group. The synthesis of the aliphatic ketones: 2-hexanone, 2-decanone, 2-octanone, 2-nonanone and 2-undecanone permitted us to amplify the Carbon-13 NMR data of these ketones and to estimate the empirical substituent effect of this group. Table 3 shows the empirical substituent effect of the CH_3CO grup (substituent chemical shift). The five empirical substituent effects α, β, γ, δ and ε are defined by comparison of the ketone chemical shift with the corresponding alkanes.

Table 1. Physical Constantes of Aliphatic Ketones

Compounds	b.p (°C/Torr)	Yield (%
2-butanone	80/760	82
2-pentanone	101/760	77
2-hexanone	38/30	76
2-heptanone	48/20	74
2-octanone	70/15	70
2-nonanone	95/30	78
2-decanone	98/20	72
2-undecanone	100/10	80

The difference is the substituent chemical shift whose average values are shown in the Table 3. These values can be useful in correlation analysis.

Table 2. Carbon-13 NMR Chemical Shifts of Aliphatic Ketones[3]

	δ (ppm)										
Compounds	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11
2-butanone	28,4	206,7	35,3	6,5							
2-pentanone	29,0	207,6	44,9	16,7	13,0						
2-hexanone	28,8	207,2	42,5	**25,2**	21,6	13,0					
2-heptanone[a]	29,6	208,4	43,7	23,6	31,5	22,6	13,9				
2-octanone	29,5	208,7	43,6	23,7	28,6	31,4	22,2	13,7			
2-nonanone[a]	28,7	207,5	43,1	23,4	28,7	28,7	31,2	22,1	13,5		
2-decanone	**28,9**	**208,0**	43,7	24,1	29,5	29,5	29,5	32,0	22,8	14,1	
2-undecanone	29,2	208,3	43,5	23,7	29,1	29,1	29,1	29,1	31,7	22,5	13,9

a = in $CDCl_3$

Table 3. Empirical Substituent Effects of Aliphatic Ketones[3]

	δ (ppm)				
Group	α	β	δ	δ	ε
MeCO	29,6	0,8	-3,2	-0,3	-0,5

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