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ESTERIFICATION SHIFTS IN CARBON-13 NMR SPECTRA OF ALCOHOLS

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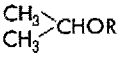
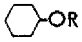
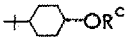
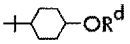
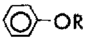
The acetylation shift in ^{1}H NMR spectroscopy, since its first report by Kawazoe and coworkers,[1] has been a useful tool for solving various kinds of problems in organic chemistry.[2] In ^{13}C NMR spectroscopy,[3] it has frequently been applied to organic chemical problems, in particular, ^{13}C signal assignments.[4] However, acetylation shift values, $\Delta\delta_C$, are generally as small as ca. 3 ppm, and sometimes the shift results become ambiguous when influenced by other factors. We have frequently encountered such ambiguities in connection with studies of 14-membered-macrolide erythromycins[5] and microbial quinone antibiotics,[6] which have several hydroxyl groups. Therefore, we examined other esterification effects upon ^{13}C chemical shifts of some fundamental alcohols and found that methoxycarbonylation (Car) and mesylation (Ms) are superior for the purpose.

The TABLE summarizes our results. The effects on α-carbon chemical shifts by the esterifications are about two (for Car) and four (for Ms) times stronger than those by acetylation (Ac), although the effects on β-carbon shifts are almost equal. The Ms shifts of γ- and δ-carbons are also larger than the other two effects. It should be emphasized that stereochemical differences were clearly observed in the esterification shifts of β- and γ-carbons between trans- and cis-tert-butylcyclohexanols (see the TABLE). These results demonstrate that the Car and Ms shifts more clearly characterize the situation of an OH group in a polyhydroxy compound than the Ac shift. These two esterifications do not disturb the upfield part of ^{13}C spectra as well as ^{1}H spectra as acetylation does. Benzoylation and tosylation shifts were very similar to Car and Ms shifts, respectively; however, the benzene-ring carbon signals sometimes disturb the downfield part of the spectra. For the sake of comparison, data on phenol are also included in the TABLE.

Some applications of the esterification shifts will be published soon.[6]

TABLE. ^{13}C Chemical Shift, δ_C, and Esterification Shift, $\Delta\delta_C$ (ppm), Data[a]

R^b				Compound			
	CH_3OR	CH_3CH_2OR	 $\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}CHOR$		[c]	[d]	
	α-Carbon						
H (δ_C)	50.0	57.9	63.9	69.9	70.9	65.6	154.8
Ac	+1.5	+2.4	+3.6	+2.7	+2.7	+3.7	-4.1
Car	+4.8	+6.2	+7.9	+6.7	+6.8	+8.1	-3.4
Ms	+6.1	+8.8	+14.0	+11.4	+11.2	+13.4	-5.4
	β-Carbon						
H (δ_C)	---	18.2	25.3	35.6	35.9	33.4	115.4
Ac	---	-3.9	-3.4	-3.8	-3.7	-2.7	+6.1
Car	---	-3.8	-3.5	-3.8	-3.8	-2.7	+5.7
Ms	---	-3.2	-2.3	-2.9	-2.7	-1.7	+6.7
	γ-Carbon						
H (δ_C)	---	---	---	24.4	25.7	21.0	129.7
Ac	---	---	---	-0.5	-0.1	+0.8	-0.4
Car	---	---	---	-0.6	-0.2	+0.6	-0.2
Ms	---	---	---	-0.9	-0.1	+1.2	+0.4
	δ-Carbon						
H (δ_C)	---	---	---	25.8	47.3	48.2	121.1
Ac	---	---	---	-0.2	0.0	-0.5	+4.5
Car	---	---	---	-0.2	-0.2	-0.5	+4.9
Ms	---	---	---	-0.9	-0.7	-0.9	+6.3
	Me-carbon						
Ac (δ_C)	20.6	20.9	21.3	21.3	21.3	21.3	21.0
Car (δ_C)	54.8	54.6	54.3	54.3	54.3	54.3	55.2
Ms (δ_C)	36.3	37.4	38.5	38.6	38.7	38.6	37.2
	CO-carbon						
Ac (δ_C)	171.4	170.9	170.4	170.3	170.3	170.3	169.0
Car (δ_C)	156.7	156.0	155.6	155.4	155.4	155.4	154.3

[a] ^1H-Noise-decoupled natural-abundance ^{13}C FT NMR spectra were recorded on a Varian NV-14 FT NMR spectrometer at 15.087 MHz using about 1 mmol cm^{-3} solutions in $CDCl_3$ and 8-mm spinning tubes at room temperatures; errors of δ_C (from internal TMS) are about ±0.1. Plus sign denotes a downfield shift.
[b] Ac = COMe; Car = CO_2Me; Ms = SO_2Me. [c] $\delta_C(\underline{Me}_3C-)$ 27.6 and $\delta_C(Me_3\underline{C}-)$ 32.2. [d] $\delta_C(\underline{Me}_3C-)$ 27.5 and $\delta_C(Me_3\underline{C}-)$ 32.6.

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