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Preliminary communication

A carbon-13 NMR spectroscopic study of ferrocenylmethyl carbonium ions

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SUMMARY

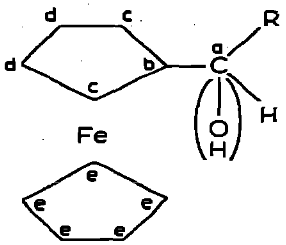
The ^{13}C NMR spectra of three ferrocenylmethyl carbonium ions and of the alcohols from which they were derived have been obtained. The chemical shifts and coupling constants of the carbonium ions are explicable in terms of a structure that has the positive charge extensively delocalized throughout the entire molecule, with a fulvene-like structure for the substituted cyclopentadienyl ring.

In connection with a study of tricobaltcarbon-substituted carbonium ions[1] it was noted that the proton NMR spectra of these cations closely resembled the proton NMR spectra of similar ferrocenylmethyl carbonium ions as far as the signals due to the proton substituents on the carbonium ion centers were concerned. Since ^{13}C NMR spectra provide a clearer picture of the electron distribution within molecules than do proton NMR spectra, we undertook a ^{13}C NMR study of $C_5H_5FeC_5H_4$- and $(OC)_9Co_3C$-substituted carbonium ions. In this paper we report our results obtained on the former species.

The extraordinarily high stability of ferrocenylmethyl carbonium ions has generated considerable interest and much speculation as to the origin of their stability (ref. 2 and earlier references cited therein). We have studied the ^{13}C NMR spectra of $C_5H_5FeC_5H_4\overset{+}{C}HR$ [I, R = H; II, R = CH_3; and III, R = C_6H_5] and of the alcohols from which these were derived, $C_5H_5FeC_5H_4CH(OH)R$ [IV, R = H; V, R = CH_3; VI, R = C_6H_5]. The shifts were obtained in the Fourier transform mode utilizing a Bruker HFX-90 spectrometer interfaced with a Digilab FTS/NMR-3 data system and are accurate to ± 0.1 ppm. The alcohols were dissolved in $CDCl_3$ and their shifts are relative to internal tetramethylsilane (TMS) (Table 1; positive values indicate decreased shielding relative to TMS). For the carbonium ion spectra, the alcohols were dissolved in conc. H_2SO_4, with cooling and under dry nitrogen, conditions which are essential for the success of the experiment.

TABLE 1

CARBON-13 CHEMICAL SHIFTS AND COUPLING CONSTANTS OF SOME FERROCENYLMETHYL ALCOHOLS AND DERIVED CARBONIUM IONS



R	Carbon	Alcohol	J(C–H)	Carbonium Ion	J(C–H)	Δδ
H	a	60.6	140	86.8	165	26.2
	b	88.1	–	109.6	–	21.5
	c	68.2	175	83.6	185	15.4
	d	68.2	175	93.5	185	25.3
	e	68.2	175	81.4	185	13.2
CH_3	a	65.5	145	117.6	165	52.1
	b	94.7	–	104.8	–	10.1
	c }[a]	66.0	170	80.0	185	14.0
	c	66.2	170	80.9	185	14.7
	d }[a]	67.7	175	93.1	178	25.4
	d	67.7	175	93.4	178	25.7
	e	68.3	175	81.5	185	13.2
	CH_3	23.6	123	19.0	130	–4.6
C_6H_5	a	72.1	145	121.5	160	49.4
	b	94.1	–	101.2	–	7.1
	c }[a]	66.1	175	79.5	183	13.4
	c	67.4	175	81.8	183	14.4
	d }[a]	68.0	175	92.8	185	24.8
	d	68.0	175	93.7	185	25.7
	e	68.5	175	82.6	180	14.1
	Ph C(1)	143.5	–	133.7	–	–9.8
	Ph C(2) }[a]	126.3	155	130.2	150	3.9
	Ph C(3)	128.2	155	130.2	150	2.0
	Ph C(4)	127.4	155	133.4	150	6.0

[a] No attempt was made to distinguish between these resonance for specific assignments.

Chemical shifts of the carbonium ions are given relative to external TMS (Table 1).

The assignments of the resonances shown in Table 1 were based on standard ^{13}C NMR correlations[3] and on proton-coupled spectra, from which the listed coupling constants (± 2 Hz) were obtained. The assignments for carbons c and d in II, III, V and VI were based on the non-equivalence of the two nuclei labelled c and the two nuclei labelled d. (This non-equivalence arises in the alcohols from the presence of an asymmetric center and in the cations from the lack of free rotation about the C_a—C_b bond. Because the non-equivalence of these nuclei is a direct result of the presence of a substituent on the ring, the pair of resonances with the greater separations were assigned to the pair of nuclei, nearer the substituent.

There are three notable features of the chemical shifts observed. First, the value of $\Delta\delta$ for carbon a, the change in chemical shift of the carbinyl carbon atom observed on conversion of the respective alcohol to the carbonium ion, is relatively small in all three systems. In comparison, $\Delta\delta$ for the $Me_2CHOH/Me_2\overset{+}{C}H$ system is 255.3 ppm[4]. Thus the unusual stabilities of ferrocenylmethyl carbonium ions are manifested in the chemical shifts of carbon a. Second, the sum of $\Delta\delta$ for the entire molecule is approximately 200 ppm for each system, while for classical carbonium ions this sum is ~400 ppm[4]. Consequently, a portion of the charge appears to be borne by the iron atom. Third, in the ferrocenylmethylcarbonium ions the $\Delta\delta$ for carbons e is approximately the same as for carbons c, implying that the amount of charge delocalization in the two C_5 rings is approximately the same. (The higher $\Delta\delta$ for carbons d will be examined below.)

The trends observable in Table 1 are consistent with general ^{13}C NMR correlations and substituent effects[3] and are best explained in terms of a model in which the iron atom is symmetrically bonded to a cyclopentadienyl ligand and is also bonded to a fulvene-like ligand. The alcohol and carbonium ion chemical shifts reported in Table 1 show striking parallels with the ^{13}C spectral data in the series CH_3CH_2OH, $(CH_3)_2CHOH$ and $CH_3(Ph)CHOH$[5] and $CH_2{=}CH_2$, $CH_3CH{=}CH_2$ and $PhCH{=}CH_2$[6], respectively. The trend for carbon a in the $C_5H_5FeC_5H_4CHR$ cations; R = H (most shielded), R = CH_3, R = Ph (least shielded), is typical of substituted olefins and is observed in the series of olefins mentioned above. The ordering for carbon a in the alcohols $C_5H_5FeC_5H_4CH(OH)R$ follows the order for ethanol, 2-propanol, 1-phenylethanol. Furthermore, $\Delta\delta$ in going from the alcohol to the carbonium ion in the ferrocenylmethyl series is paralleled in the two model series: $CH_2OH/CH_2 < CH(OH)Ph/CHPh < CH(OH)CH_3/CHCH_3$. For carbon b in the ferrocenylmethyl cations the unsubstituted derivative is the least shielded and the phenyl-substituted derivative the most shielded. This trend also is consistent with the fulvene-like structure, as demonstrated by the continual increase in the shieldings of the CH_2 carbon atoms in the model series $CH_2{=}CH_2$, $CH_3CH{=}CH_2$, $PhCH{=}CH_2$. Also, the methyl and C(1) phenyl carbon atoms both are more shielded in II and III than in the corresponding alcohols, V and VI. For the model series, the same nuclei are more shielded in propene and styrene than in their corresponding alcohols. Finally, the sp^2 hybridization clearly indicated by the observed coupling constant for carbon a in I, II and III further supports a fulvene-like structure and is not consistent with any model in which C_a has a significant amount of sp^3 character resulting from σ bonding with the iron atom.

While the above observations do not require the postulation of extensive movement of the iron atom with respect to its position in the alcohol when the carbonium ion is formed, one might expect such movement to occur in some degree in order to facilitate more effective overlap of the appropriate iron orbitals with those of the fulvene-like ligand. The chemical shifts of carbon atoms c and d suggest that just such a shift does in fact occur.

Carbon atoms c are shifted, on the average, ca. 14 ppm in going from the alcohols to the cations, while carbon atoms d are shifted, on the average, ca. 25 ppm. Bonding of olefinic carbon atoms to iron results in a shielding of from 45 to 75 ppm (compare butadiene and its $Fe(CO)_3$ complex[7]). Were the iron atom in I, II and III shifted away from the d carbon atoms and toward carbon atom a (relative to its position in the alcohols), then the d carbon atoms would be less able to bond effectively with the iron atom. The increased shift (greater deshielding) of these carbon atoms, relative to C_c and C_e, indicate that the position of the iron atom with respect to the substituted cyclopentadienyl ring has changed in going from the alcohols to the carbonium ions.

In summary, this study has suggested that the high stability of the ferrocenylmethyl carbonium ions has its origin in the extensive delocalization of charge throughout the whole carbon skeleton and, to some (unknown) extent, to sharing of the charge by the iron atom. This is in good accord with the models for such carbonium ions favored by Richards and Cais and their respective collaborators on the basis of proton NMR and Mössbauer spectroscopic studies[2,8], and ESCA measurements[9].

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