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PMR AND ELECTRONIC SPECTRA OF SOME α -CYMANTRENYLCARBENIUM IONS

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Summary

PMR and UV spectra, in acid media, of some α -cymantrenylcarbenium ions are reported. The data obtained proves that the nature of the stabilisation of the positive charge is common to both cymantrenylcarbenium and ferrocenylcarbenium ions. Also reported are the values of pK_R^+ for the equilibrium $(CO)_3MnC_5H_4CR(R')(OH) \rightleftharpoons (CO)_3MnC_5H_4CR(R')$, ($R = H, CH_3, C_6H_5$; $R' = C_2H_5, C_6H_5, p-C_6H_4OCH_3$).

The mechanism by which the cationic centre attached to the metallocenyl radical is stabilised is of great interest but has not yet been reported. It may be suggested that comparison of metallocenylcarbenium ions, which differ by the nature of the transition metal and ligands, should reveal some aspects of the problem. However, apart from α -ferrocenylcarbenium ions, which have been studied intensively [1,2], the metallocenylic carbenium ions have not attracted much attention [3–5].

For a long time the only example of α -cymantrenyl cations appeared to be the stable dication $(CO)_3MnC_5H_4-\dot{C}H-C_6H_4-\dot{C}H-C_5H_4Mn(CO)_3$, reported by Cais [6]. Recently, Ginsburg, Setkina and Kursanov [7] demonstrated the existence of the α -cymantrenylcarbenium ions $LL'(CO)MnC_5H_4-\dot{C}RR'$, where L and L' are carbonyl or phosphine, formed from corresponding carbinols in a $CF_3COOH-CH_2Cl_2$ mixture.

Results and discussion

This paper describes the results of systematic investigations on the behaviour of α -cymantrenylcarbinols (I) in neutral and acid media, by application of PMR and electronic spectroscopic methods.

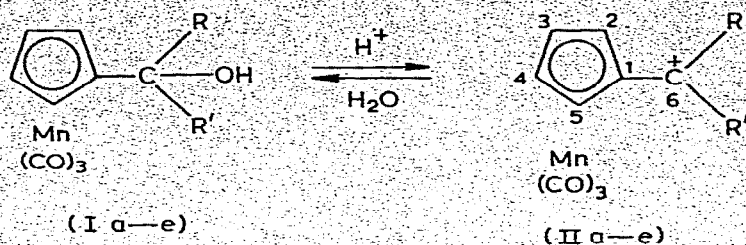
Table 1 shows the PMR spectra of Ia–e in CCl_4 solutions. The presence of the chiral centres in Ia–d leads to a difference in chemical shifts for diastereotopic protons in positions 2,5 of the cyclopentadienyl ring [8].

TABLE 1

THE PMR SPECTRA OF CYMANTRENYLCARBINOLS Ia-e AND METHYLPHENYLFERROCENYL-CARBINOL (III) IN CCl₄ SOLUTION (0.4 M, δ (ppm) from internal TMS, 60 MHz, multiplicity in parentheses)

R	R'	H(2,5) ^a	H(3,4) ^a	OH	CH ₃	C ₆ H ₅	CH ₂ CH ₃	CH ₂ CH ₃	C ₆ H ₄	OCH ₃	CHOH	C ₅ H ₅
CH ₃	CH ₂ CH ₃ (Ia)	4.76; 4.94 (m)	4.61 (m)	1.51 (s)	1.41 (s)		1.72 (q)	0.92 (t)				
H	C ₆ H ₅ (Ib)	4.63; 4.88 (m)	4.58 (m)	2.21 (d)		7.25 (s)					5.36 (d)	
CH ₃	C ₆ H ₅ (Ic)	4.82; 4.89 (m)	4.51 (t)	1.97 (s)	1.79 (s)	7.31 (m)						
C ₆ H ₅	p-C ₆ H ₄ OCH ₃ (Id)	4.84 (m)	4.64 (t)	2.41 (s)		7.33 (s)			6.79-7.3 (m)	3.83 (s)		
C ₆ H ₅	C ₆ H ₅ (Ie)	4.74 (t)	4.53 (t)	2.35 (s)		7.15 (s)						
CH ₃	C ₆ H ₅ (III)	3.95-4.35 (m)		2.38 (s)	1.77 (s)	7.23 (m)						4.18 (s)

^a Shift assignments for the ring protons of Ia-e have been based upon studying the effects of adding Eu(fod)₃ and Dy(fod)₃ on the signal positions.



- a $R = \text{CH}_3$, $R' = \text{C}_2\text{H}_5$
 b $R = \text{H}$, $R' = \text{C}_6\text{H}_5$
 c $R = \text{CH}_3$, $R' = \text{C}_6\text{H}_5$
 d $R = \text{C}_6\text{H}_5$, $R' = p\text{-C}_6\text{H}_4\text{OCH}_3$
 e $R = \text{C}_6\text{H}_5$, $R' = \text{C}_6\text{H}_5$

When CCl_4 was replaced by sulphuric or trifluoroacetic acids or their mixture, considerable changes in the PMR spectra were observed. The values of the chemical shifts in concentrated H_2SO_4 solutions are given in Table 2. These data demonstrate that all chemical shifts appear downfield from the signals due to the corresponding alcohol precursors in CCl_4 solutions, the most significant effects being observed for the ring protons ($\delta = 4.5\text{--}5.0$ ppm in CCl_4 , $5.5\text{--}6.3$ ppm in H_2SO_4), for the protons of the α -methyl groups ($1.4\text{--}1.8$ ppm in CCl_4 , $2.5\text{--}2.9$ ppm in H_2SO_4) and also for the methyne proton of the alcohol Ib (5.36 ppm in CCl_4 , 7.40 ppm in H_2SO_4). The character of the changes in the PMR spectra of α -cymantrenylcarbinols Ia–e, which occur by replacing CCl_4 by concentrated sulphuric acid, is similar to that observed by the formation of α -ferrocenylcarbenium ions from the corresponding alcohols (Table 1, 2 and [9]). Therefore the data reported reveal the formation of carbenium ions II when cymantrenylcarbinols Ia–e are dissolved in concentrated H_2SO_4 .

The PMR spectra of alcohols Ib–e in trifluoroacetic acid are quite similar to those in H_2SO_4 , except for some changes in the positions of signals, probably due to an effect of the medium. In the case of Ia, the spectra in concentrated H_2SO_4 and CF_3COOH differ significantly (Fig. 1). However, if sulphuric acid is added to the trifluoroacetic acid solution of methylethylcymantrenylcarbinol (Ia) the same spectrum as that observed in pure H_2SO_4 results. As sulphuric acid is a stronger acid than CF_3COOH (at least in the terms of H_0 [10]) one may assert that in concentrated H_2SO_4 the carbinols Ia–e are converted into corresponding α -cymantrenylcarbenium ions IIa–e.

A fine feature of the PMR spectra of cations IIa–c, formed from the chiral alcohols Ia–c, was the retention of the unequivalence of the ring protons. We observed three signals due to ring protons ($5.4\text{--}6.3$ ppm): two signals of one proton intensity at weaker fields which can be assigned to the protons in the 2 and 5 positions, by analogy with ferrocenylcarbenium ions [1,9], and a signal of two protons intensity due to protons in the 3, 4 positions. This feature is known for ferrocenylcarbeniums and assigned to braking of rotation about the $\text{C}_1\text{--C}_6$ bond ([9] and Table 2). This creates the planar chirality and as a result diastereotopy and anisochonity of the ring protons having the same chemical surroundings.

TABLE 2

THE PMR SPECTRA OF CYMANTRENYLCARBINOLS Ia-e, PHENYL- AND METHYLPHENYL-FERROCENYLCARBINOLS (IV AND III) IN CONCENTRATED H₂SO₄ (0.8 M, δ (ppm) from internal TMS, 60 MHz, multiplicity in parentheses)

P	R'	H(2,5) ^d	H(3,4) ^d	CH	C ₆ H ₅	CH ₃	CH ₃ CH ₃	CH ₂ CH ₃	C ₆ H ₄	OCH ₃	C ₅ H ₅
CH ₃	CH ₂ CH ₃ (Ia)	5.70; 5.78 (m)	6.25 (m)			2.51 (s)	2.62 (q)	1.46 (t)			
H	C ₆ H ₅ (Ib) ^b	5.91; 5.45 (m)	6.12 (m); 5.91 (m)	7.40 (e)	7.19 (m)						
CH ₃	C ₆ H ₅ (Ic)	5.73; 5.16 (m)	6.34 (m)		7.88 (m)	2.88 (s)					
C ₆ H ₅	p-C ₆ H ₄ OCH ₃ (Id)	5.72; 5.88 (m)			7.62 (m)				7.1-8.1 (m)	4.22 (s)	
C ₆ H ₅	C ₆ H ₅ (Ie)	5.87 (m)	6.23 (m)		7.61 (m)						
CH ₃	C ₆ H ₅ (III)	4.76; 5.18 (m)	6.24 (m)		7.55 (m)	2.29 (s)					4.71 (s)
H	C ₆ H ₅ (IV) ^c	4.77, 5.52	6.24; 6.45	8.09	7.4-7.9						4.86

^d Shift assignments are assigned analogously to those of ferrocenylcarbenium ions [1,9].

^b The spectrum is recorded on Varian HA-100 instrument.

^c Ref. [9].

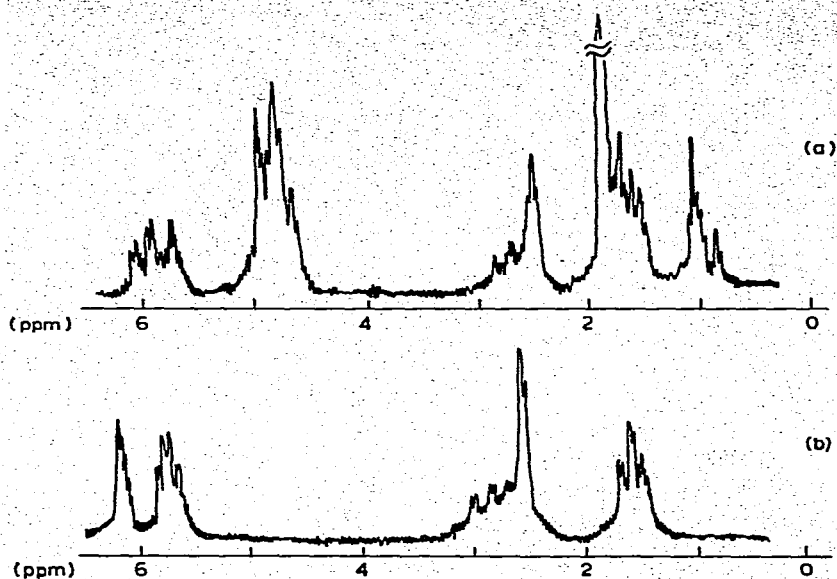


Fig. 1. PMR spectra of Ia with TMS as external standard: (a) in CF_3COOH ; (b) in concentrated H_2SO_4 . The difference, $\Delta\delta$, between internal and external TMS in CF_3COOH is -0.52 ppm.

The similarity of the PMR spectra of cymantrenyl- and ferrocenyl-carbenium ions, as in the nearness of positions of the signals due to similar nuclei and the observation of the planar chirality, allows us to suggest that the stabilisation of the adjacent cationic centre in these isoelectronic structures occurs by a common mechanism.

The UV data confirm the formation of cations II on dissolving cymantrenyl-carbinols (I) in the acids. The ethanol solutions of carbinols Ia–e absorb in the 330 nm region, characteristic for cymantrene compounds. When the solvent is changed for acids (H_2SO_4 , CF_3COOH , HClO_4) a rise in the absorption occurs at longer wavelength. Table 3 shows the λ_{max} and $\log \epsilon$ values in the UV spectra of carbinols Ia–e in concentrated sulphuric acid solutions. The electronic spectra of cymantrenylcarbinols in trifluoroacetic acid are quite similar to those in concentrated H_2SO_4 . However, the intensities of the signals for Ia in CF_3COOH

TABLE 3

ELECTRONIC SPECTRA OF THE SOLUTIONS OF CYMANTRENYLCARBINOLS Ia–e IN CONCENTRATED H_2SO_4 AND MAGNITUDES OF $\text{p}K_{\text{R}}^+$ VALUES

Carbinol	Ia	Ib	Ic	Id ^a	Ie
λ_{max} ($\log \epsilon$)	345(3.39), 416(3.45)	346(3.99), 421(3.88)	357(3.99), 455(3.75)	264(3.80), 379(4.08), 446(4.47), 611(4.13) ^b	390(4.32), 611(3.84)
$\text{p}K_{\text{R}}^+$ (λ_{max})	9.4(416)	8.7(421)	8.3(455)	4.9(446) ^b	6.5(390) ^b
Solution colour	Dark orange		Brown red	Green	Blue

^a In CF_3COOH solution.

^b In aqueous HClO_4 .

is about 1.5 times lower than those in Table 3. Therefore both spectral methods prove that the carbinol Ia in trifluoroacetic acid, apart from the other alcohols studied, only partially forms carbenium ion IIa.

It should be emphasised that the solutions of α -cymantrenyl cations have a high stability; the features of the UV spectra did not change on keeping the CF_3COOH and HClO_4 (57%) solutions in air for a long time. The sulphuric acid solutions are also stable, but we failed to record the initial spectrum for the compound Id, probably because of by-processes. On standing the solution of Id its UV spectrum showed an absorption of high intensity at $\lambda_{\text{max}} = 475$ nm and the bands at $\lambda_{\text{max}} = 446$ and 611 nm disappeared.

It is known that dimethylferrocenylcarbinol and even unsubstituted ferrocenylcarbinol form completely the corresponding carbenium ions in trifluoroacetic acid [9,11]. The fact that methylethylcymantrenylcarbinol (Ia) only partially forms the cation IIa, on dissolving the carbinol in CF_3COOH , means that the radical $(\text{CO})_3\text{MnC}_5\text{H}_4$ possesses less ability to stabilise the adjacent cationic centre than the ferrocenyl residue. We have confirmed this qualitative conclusion by measuring $\text{p}K_{\text{R}}^+$ values for the equilibrium $\text{I} \rightleftharpoons \text{II}$. The values obtained show that the $(\text{CO})_3\text{MnC}_5\text{H}_4$ radical stabilises the cationic centre more effectively than the phenyl, but much less than the ferrocenyl radical. The $\text{p}K_{\text{R}}^+$ value for carbinol Ib is equal to -8.7 and those for diphenyl- and phenylferrocenylcarbinols, -13.3 [12] and -0.4 [13] respectively.

Experimental

A Perkin-Elmer R-20 NMR spectrometer was used to obtain the PMR spectra. The sulphuric and trifluoroacetic acid solutions of the carbinols were prepared by adding the carbinol species to the acids while vigorously stirring and cooling to 0°C in an argon atmosphere. The electronic spectra were recorded on Specord-UV-VIS (Carl-Zeis) spectrophotometer with $\sim 10^{-4}$ M solutions of the alcohols in acids.

The $\text{p}K_{\text{R}}^+$ values were measured by the standard method [12] employing the H_{R}^+ values for H_2SO_4 and HClO_4 acids at the half ionisations of the carbinols.

The tertiary carbinols Ia, c-e and III were obtained by Grignard reaction of acetyl- and benzoyl-cymantrenes and acetylferrocene with the corresponding Grignard reagents as previously described [14]. Phenylcymantrenylcarbinol was prepared by the reduction of benzoylcymantrene with LiAlH_4 [15]. The carbinols not previously reported were characterised and the results shown in

TABLE 4
ANALYTICAL DATA OF NOVEL CARBINOLS

Carbinol	Yield (%)	B.p. ($^\circ\text{C}$ mm Hg)	M.p. ($^\circ\text{C}$)	n_{D}^{20}
Ia	60	$95/3 \times 10^{-2}$		1.5746
Ic	78	$142/5 \times 10^{-2}$	46-47	1.6195
Id	79		108-110 (from hexane)	
III	76		111-113 (from hexane)	

Table 4. The elemental analyses agreed with the calculated data. A mass spectrometric technique was applied to determine molecular weights.

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