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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  $\alpha$ -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  $\alpha$ -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  $\alpha$ -cymantrenyl cations appeared to be the stable dication (CO)<sub>3</sub>MnC<sub>5</sub>H<sub>4</sub>—CH—C<sub>6</sub>H<sub>4</sub>—CH—C<sub>5</sub>H<sub>4</sub>Mn(CO)<sub>3</sub>, reported by Cais [6]. Recently, Ginsburg, Setkina and Kursanov [7] demonstrated the existence of the  $\alpha$ -cymantrenylcarbenium ions LL'(CO)MnC<sub>5</sub>H<sub>4</sub>—CRR', where L and L' are carbonyl or phosphine, formed from corresponding carbinols in a CF<sub>3</sub>COOH—CH<sub>2</sub>Cl<sub>2</sub> mixture.

## Results and discussion

This paper describes the results of systematic investigations on the behaviour of  $\alpha$ -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<sub>4</sub> 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 Is—e AND METHYLPHENYLFERROCENYLCARBINOL (III) IN CCIA SOLUTION (0.4 M. 8. (DPm). from internal TMS, 60 MHz, multiplicity in parentheses)

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t 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.

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 ( $\delta = 4.5-5.0$  ppm in  $CCl_4$ , 5.5-6.3 ppm in  $H_2SO_4$ ), for the protons of the  $\alpha$ -methyl groups (1.4–1.8 ppm in  $CCl_4$ , 2.5–2.9 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  $\alpha$ -cymantrenylcarbinols Ia—e, which occur by replacing  $CCl_4$  by concentrated sulphuric acid, is similar to that observed by the formation of  $\alpha$ -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  $\alpha$ -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 (5.4-6.3 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  $C_1-C_6$  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 1a-e, PHENYL- AND METHYLPHENYL-FERROGENYLCARBINOLS (IV AND III) IN CONCENTRATED H2SO4 (0.6 M.5 (ppm) from internal TMS, 60 MHz, multiplicity in parentheses)

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C <sub>6</sub> H <sub>5</sub>	7.19 (m) 7.83 (m) 7.62 (m) 7.61 (m) 7.56 (m) 7.44—7.9
C,H,S	7.19 (m) 7.83 (m) 7.62 (m) 7.61 (m) 7.55 (m) 7.4—7.9
C6H5	7.19 (m) 7.83 (m) 7.62 (m) 7.61 (m) 7.56 (m)
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HO	6.25 (m) 6.12 (m); 7.40 (s) 6.91 (m) 6.34 (m) 6.23 (m) 6.24 (m) 6.24; 6.45 8.09
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I(2,6) 4 H(3,4) 4 CH	6.70: 6.78 (m) 6.25 (m) 6.91: 6.45 (m) 6.12 (m); 7.40 (s) 6.91 (m) 6.91 (m) 6.73: 6.16 (m) 6.34 (m) 6.23 (m) 6.23 (m) 4.76: 5.18 (m) 6.24 (m) 4.77: 5.52 6.24 (m)
I(2,6) 4 H(3,4) 4 CH	6.70: 6.78 (m) 6.25 (m) 6.91: 6.45 (m) 6.12 (m); 7.40 (s) 6.91 (m) 6.91 (m) 6.73: 6.16 (m) 6.34 (m) 6.23 (m) 6.23 (m) 4.76: 5.18 (m) 6.24 (m) 4.77: 5.52 6.24 (m)
I(2,6) 4 H(3,4) 4 CH	6.70: 6.78 (m) 6.25 (m) 6.91: 6.45 (m) 6.12 (m); 7.40 (s) 6.91 (m) 6.91 (m) 6.73: 6.16 (m) 6.34 (m) 6.23 (m) 6.23 (m) 4.76: 5.18 (m) 6.24 (m) 4.77: 5.52 6.24 (m)
I(2,6) 4 H(3,4) 4 CH	6.70: 6.78 (m) 6.25 (m) 6.91: 6.45 (m) 6.12 (m); 7.40 (s) 6.91 (m) 6.91 (m) 6.73: 6.16 (m) 6.34 (m) 6.23 (m) 6.23 (m) 4.76: 5.18 (m) 6.24 (m) 4.77: 5.52 6.24 (m)
I(2,6) 4 H(3,4) 4 CH	6.70: 6.78 (m) 6.25 (m) 6.91: 6.45 (m) 6.12 (m); 7.40 (s) 6.91 (m) 6.91 (m) 6.73: 6.16 (m) 6.34 (m) 6.23 (m) 6.23 (m) 4.76: 5.18 (m) 6.24 (m) 4.77: 5.52 6.24 (m)
I(2,6) 4 H(3,4) 4 CH	6.70: 6.78 (m) 6.25 (m) 6.91: 6.45 (m) 6.12 (m); 7.40 (s) 6.91 (m) 6.91 (m) 6.73: 6.16 (m) 6.34 (m) 6.23 (m) 6.23 (m) 4.76: 5.18 (m) 6.24 (m) 4.77: 5.52 6.24 (m)
I(2,6) 4 H(3,4) 4 CH	m) 6.25 (m) m) 6.12 (m); 7.40 (s) 5.91 (m) m) 6.34 (m) m) 6.23 (m) m) 6.24 (m) e.24 (m)
I(2,6) 4 H(3,4) 4 CH	6.70: 6.78 (m) 6.25 (m) 6.91: 6.45 (m) 6.12 (m); 7.40 (s) 6.91 (m) 6.91 (m) 6.73: 6.16 (m) 6.34 (m) 6.23 (m) 6.23 (m) 4.76: 5.18 (m) 6.24 (m) 4.77: 5.52 6.24 (m)
I(2,6) 4 H(3,4) 4 CH	CH2CH3 (Ia)     5.70: 5.78 (m)     6.25 (m)       O6H5 (Ib)     5.91: 5.46 (m)     6.12 (m);     7.40 (s)       O6H5 (Ia)     6.73: 6.16 (m)     6.34 (m)       P.C6H4 OCH3 (Id)     5.72: 5.88 (m)     6.24 (m)       C6H5 (II)     6.87 (m)     6.23 (m)       C6H5 (III)     4.76: 5.18 (m)     6.24 (m)       C6H5 (IV)     4.77: 5.52     6.24; 6.45     8.09
I(2,6) 4 H(3,4) 4 CH	CH2CH3 (Ia)     5.70: 5.78 (m)     6.25 (m)       O6H5 (Ib)     5.91: 5.46 (m)     6.12 (m);     7.40 (s)       O6H5 (Ia)     6.73: 6.16 (m)     6.34 (m)       P.C6H4 OCH3 (Id)     5.72: 5.88 (m)     6.24 (m)       C6H5 (II)     6.87 (m)     6.23 (m)       C6H5 (III)     4.76: 5.18 (m)     6.24 (m)       C6H5 (IV)     4.77: 5.52     6.24; 6.45     8.09
I(2,6) 4 H(3,4) 4 CH	CH2CH3 (Ia)     5.70: 5.78 (m)     6.25 (m)       O6H5 (Ib)     5.91: 5.46 (m)     6.12 (m);     7.40 (s)       O6H5 (Ia)     6.73: 6.16 (m)     6.34 (m)       P.C6H4 OCH3 (Id)     5.72: 5.88 (m)     6.24 (m)       C6H5 (II)     6.87 (m)     6.23 (m)       C6H5 (III)     4.76: 5.18 (m)     6.24 (m)       C6H5 (IV)     4.77: 5.52     6.24; 6.45     8.09
H(8,4) <sup>4</sup> CH	6.70: 6.78 (m) 6.25 (m) 6.91: 6.45 (m) 6.12 (m); 7.40 (s) 6.91 (m) 6.91 (m) 6.73: 6.16 (m) 6.34 (m) 6.23 (m) 6.23 (m) 4.76: 5.18 (m) 6.24 (m) 4.77: 5.52 6.24 (m)

d Shiff assignments are assigned analogously to those of ferrocenylcarbentum ions [1,9].
The spectrum is recorded on Varian HA-100 instrument.
C Ref. [9].

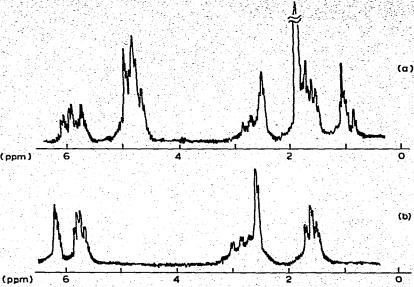


Fig. 1. PMR spectra of Ia with TMS as external standard: (a) in CF<sub>3</sub>COOH; (b) in concentrated H<sub>2</sub>SO<sub>4</sub>. The difference,  $\Delta\delta$ , between internal and external TMS in CF<sub>3</sub>COOH is -0.52 ppm.

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  $\lambda_{max}$  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 is— $\epsilon$  in concentrated  $H_2SO_4$  and magnitudes of  $dK_R^+$  values

Carbinol l	la .	<b>Tb</b>	Ic	Id <sup>a</sup>	Ie
	345(3.39), 416(3.45)			264(3.80), 379(4.08).	390(4.32), 611(3.84)
	*100.30	*21(0.06)		446(4.47),	
- TP (At more)	9.4(416) Dark orange	8.7(421)	8.3(455)	611(4.13) 4.9(446) Green	6.5(390) <sup>b</sup>

a In CF3COOH solution.

In aqueous HClO4

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  $\alpha$ -cymantrenyl cations have a high stability; the features of the UV spectra did not change on keeping the CF<sub>3</sub>COOH and HClO<sub>4</sub> (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  $\lambda_{max} = 475$  nm and the bands at  $\lambda_{max} = 446$  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  $(CO)_3MnC_5H_4$  possesse less ability to stabilise the adjacent cationic centre than the ferrocenyl residue. We have confirmed this qualitative conclusion by measuring  $pK_R^+$  values for the equilibrium  $I \rightleftharpoons II$ . The values obtained show that the  $(CO)_3MnC_5H_4$  radical stabilises the cationic centre more effectively than the phenyl, but much less than the ferrocenyl radical. The  $pK_R^+$  value for carbinol Ib is equal to -8.7 and those for diphenyl- and phenyl-ferrocenylcarbinols, -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  $0^{\circ}$ 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  $pK_R^+$  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<sub>4</sub> [15]. The carbinols not previously reported were characterised and the results shown in

TABLE 4
ANALYTICAL DATA OF NOVEL CARBINOLS

Carbinol Yield B.p. (°C mm Hg) M.p. (°C) $n_{ m D}^{20}$	
	시민 시장 : 그 그리고 없었다.
장면상 探測 살아 없는데 나는 사람들이 있었다. 그 사람들은 사람들은 그렇게 가장하게 되었다. 나는 그는 사람들은 사람들은 사람들이 되었다.	746 195

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

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