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Preliminary communication

Steric relations and the PMR spectra of monosubstituted derivatives of cymantrene having a chiral centre in the substituent

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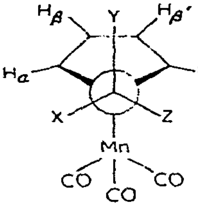
Recently some of the present authors reported on the non-equivalence of α-protons in the ring of 1,1,1-trifluoro-2-oxyethylcymantrene, (I), observed in the PMR spectrum of this compound[1]. We now report new material concerning this problem.

The ring protons of monosubstituted derivatives of cymantrene, (CMT), usually appear in the PMR spectrum as a multiplet specific to AA'BB' spin systems depending upon the nature of the substituent[2]. Such types of signal systems are due to magnetic non-equivalence of the ring protons with respect to spin–spin coupling. Some monoalkyl CMT compounds whose ring protons appear in the form of a single signal make an exception[3]. Analysis of steric relations for the ring protons of monosubstituted CMT derivatives led to the conclusion that the presence of a chiral centre in the substituent results in diastereotopy of the α and α'as well as the β and β'protons. It is natural that the diastereotopic protons should possess different physical and chemical properties analogously to a pair of diastereomers and therefore one may expect different chemical shifts for α and α' as well as β and β' ring protons in the PMR spectrum.



In the study of PMR spectra of 1-phenyloxymethylcymantrene, (II), the diethyl ester of 1-cymantryl-1-oxyethylphosphonic acid, (III), and the di-n-butyl ester of 1-cymantryloxyethylphosphonic acid, (IV), we revealed two signals from α protons of the ring with chemical shifts differing by 15 Hz. As an illustration Fig. 1a shows the PMR spectrum of 1,1,1-trifluoro-2-oxyethylcymantrene (I). Parameters of the PMR spectra of the compounds investigated are listed in Table 1.

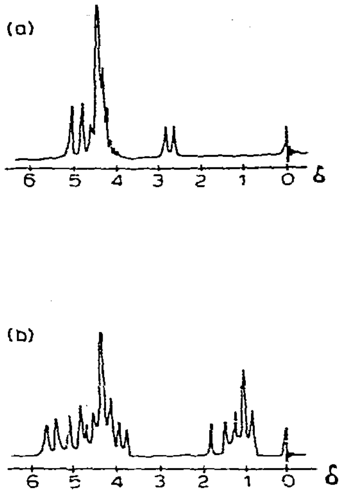


Fig.1. The PMR spectra of: (a), 1,1,1-trifluoro-2-oxyethylcymantrene; and (b), the diethyl ester of 1-cymantryloxyethylphosphonic acid.

Diastereotopic relations between the α and α' as well as β and β' protons are a necessary condition for observing the difference in the chemical shifts. However, the chemical shift difference is determined by the different degrees of shielding of the diastereotopic protons and thus it may change on going from one compound to the other. For example, the ring proton spin system in chiral 1-methyl-1-cymantrylcarbinol, (V), shows a PMR spectral pattern similar to that of non-chiral monosubstituted CMT compounds, *viz.*, two pseudo-triplets at δ 4.78 and 4.61 ppm. On the other hand, the difference between the chemical shifts of diastereotopic protons in (III) and (IV) is maximum for the compounds discussed and the non-equivalence is observed not only for the α but also for β protons of the cyclopentadienyl ring (Table 1 and Fig. 1b).

Thus in the present work we have revealed the non-equivalence of chemical shifts of diastereotopic protons of the cyclopentadienyl ring in chiral monosubstituted derivatives of cymantrene.

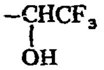
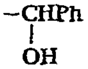
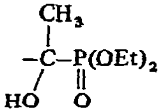
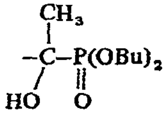
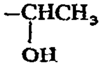
EXPERIMENTAL

Samples of the chiral alcohols (I)—(V) were prepared and purified using previously described methods[4-6]. PMR spectra were taken on Hitachi—Perkin—Elmer R—20 and Varian DA—60—IL instruments in chloroform with hexamethyldisiloxane as internal standard (δ 0.05 ppm).

TABLE 1

PMR SPECTRAL PARAMETERS[a] OF CHIRAL MONOSUBSTITUTED DERIVATIVES

OF CMT 

No	R	α,α'	β,β'	OH	O–CH
(I)	 $-\underset{\text{OH}}{\text{CH}}\text{CF}_3$	4.87 5.03	4.68	2.80	4.66 J(OH–CH) 5.5Hz
(II)	 $-\underset{\text{OH}}{\text{CH}}\text{Ph}$	4.63 4.88	4.58	2.49	5.33 J(OH–CH) 3Hz
(III)	 $-\underset{\text{HO}}{\overset{\text{CH}_3}{\text{C}}}-\underset{\text{O}}{\text{P}}(\text{OEt})_2$	4.90 5.20	4.51 4.70	3.78	J(P–OH) 12Hz
(IV)	 $-\underset{\text{HO}}{\overset{\text{CH}_3}{\text{C}}}-\underset{\text{O}}{\text{P}}(\text{OBu})_2$	4.91 5.23	4.53 4.72		
(V)	 $-\underset{\text{OH}}{\text{CH}}\text{CH}_3$	4.78	4.61	2.13	4.5 J(OH–CH) 3.96 Hz

[a] Signal assignment for the ring protons was based on ref. 2 and the assumption that the electron-attracting substituents would provide the downfield shifts of α-proton signals with respect to the β-protons. The hydroxyl and methyl protons were assigned by double nuclear resonance techniques.

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