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AN NMR STUDY OF THE CONFORMATIONS OF CERTAIN ALCOHOL DERIVATIVES OF TRICARBONYL(DIENE)IRON COMPOUNDS

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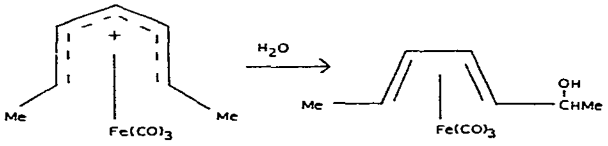
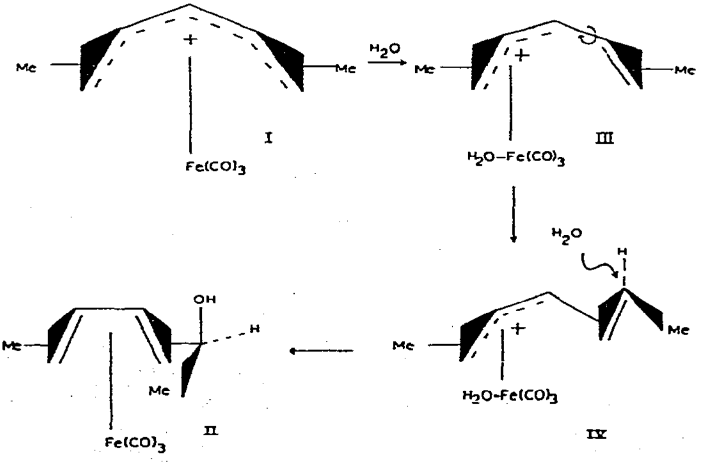
SUMMARY

An NMR study, involving lanthanide shift reagents, of the behaviour of dissymmetric alcohol derivatives of tricarbonyl(diene)iron complexes obtained by different stereospecific reactions suggests that currently assigned configurations for such compounds may perhaps not be correct.

Pettit and Mahler[1] have reported that the hydrolysis of (*syn*,*syn*-1,5-dimethylpentadienyl)iron tricarbonyl cation (I) is remarkably stereospecific, giving a racemic mixture of only one of the two possible pairs of enantiomers. On the basis of the following proposed mechanism for the hydrolysis, Pettit and Mahler[1] assigned configurations *RR* and *SS* to the enantiomers of racemic (II). Initially a hydrated vinyl-

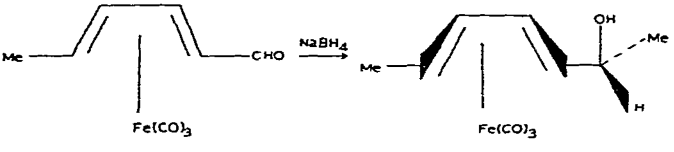


I II



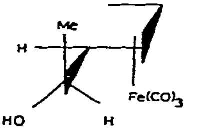
π-allyliron tricarbonyl cation (III) is formed which adopts a *trans* configuration by rotation of the C(3)–C(4) bond. A further molecule of water is assumed to attack from the diene side furthest from the tricarbonyl group. The product shown above is the *SS* form. The enantiomer of (I) having the *R* configuration likewise leads exclusively to the *RR* product. (For the purpose of assigning these configurations, each carbon of the diene is assumed to be bounded to the iron atom).

From reduction of the appropriate complexed ketones, Clinton and Lillya[2] have obtained a racemic mixture of enantiomers which are diastereoisomeric with those described above. From a consideration of detailed molecular models, these authors[2] supposed that the diastereoisomeric product alcohols exist in fixed conformations, defined largely by steric interactions involving the carbonyl groups on iron. These configurations are shown below for an *S* conformation about C(3). (The *ψ-exo*, *ψ-endo* terminology derives from the orientation of the hydroxyl function with respect to the iron tricarbonyl group). The *RR* and *SS* products therefore exist in the *ψ-exo* form, the *SR* and *RS* products being *ψ-endo*. As support for this it was suggested that the polar behaviour of the alcohol (II) from hydrolysis of the cation (I) is consistent with the "exposed" nature of the hydroxyl group. In the *ψ-endo* configuration, however, this group is sterically shielded, and indeed (V) is rather less polar than (II) estimated on the basis of the retention times of the two diastereomers on alumina and silica gel thin layers.

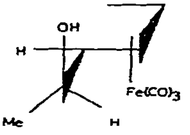


(RS product)

V

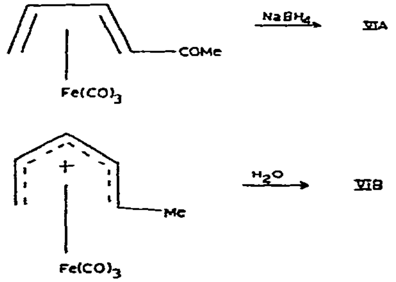


ψ-endo
(RS-form)



ψ-exo
(SS-form)

A slightly more direct approach to the problem of the conformations of the alcohols (VIA) and (VIB), which are analogous to those discussed above, using an NMR shift reagent, specifically tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octane-



dionato)europium(III), [Eu(FOD)$_3$][3], has been attempted here. Numerous reports[4,5] of the application of lanthanide shift reagents in NMR studies have appeared since the initial account by Hinckley[6]. Briefly, species having suitable functional groups, and which thereby behave as Lewis bases, form weak associations with six-coordinate lanthanide complexes. Since the associated and non-associated substrate molecules are rapidly exchanging, a time-averaged spectrum is generally observed. If the lanthanide complex is paramagnetic, the nuclear resonances of the substrate will be shifted from their normal position by an amount which depends on the relative concentration of the lanthanide complex, and on the unpaired electron spin(s) of the metal orbitals. There is a possibility that transfer of spin density from the metal to the associated substrate is minimal, in which case the shifts observed arise from a dipolar, or "pseudocontact" interaction. The amount by which a given resonance of the substrate is shifted may therefore be related to the spatial co-ordinates of the appropriate nucleus relative to those of the lanthanide metal. Generally, the observed shifts are expressed in terms of the equation of McConnell and Robertson[7]:

$$(\mathrm{PC})_i = \frac{K \cdot (3\cos^2 X_i - 1)}{R_i^3} \tag{1}$$

where $(\mathrm{PC})_i$ is the pseudocontact shift of the i-th nucleus of the complex, R_i is the length of a vector joining the i-th nucleus to the metal atom, X_i is the angle between this vector and the principal axis of the molecule. The special limitations of this equation, particularly with regard to transition metal complexes, have recently been discussed by Kurland and McGarvey[8]. Eqn. (1), whilst only approximate, has however been used with striking success by a number of authors. One approximation which is often made, and which has been shown to be quite unjustifiable[9,10], is the neglect of the angle-dependent term. In this work therefore, this term has been included as far as possible.

It should perhaps be remarked that carbonyl groups bonded to metal do not appear to interact with lanthanide shift reagents; in so far as the proton resonances of (2-methyl-1,3-butadiene)iron tricarbonyl are unperturbed by addition of Eu(FOD)$_3$. Other observations are consistent with this view[11].

The proton spectra of the alcohols (VIA) and (VIB) are very similar. Proton assignments were confirmed by spin decoupling and details of both spectra are given in Table 1. The coupling constants appear to be the same for both compounds, there are however detectable differences in the chemical shifts.

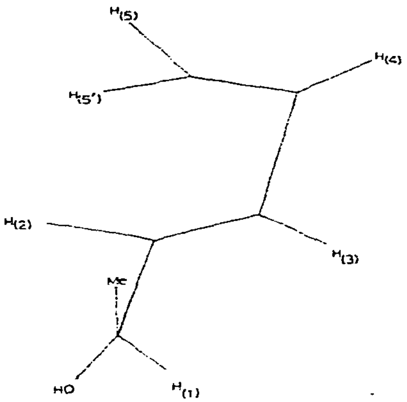
On adding anhydrous Eu(FOD)$_3$, the proton resonances of both (VIA) and (VIB) are shifted downfield to some extent. Spectra were run for each compound with increasing amounts of shift reagent, the concentration of which was estimated by integrating the FOD ligand peak which appears slightly downfield of TMS. A plot of the shift of any given resonance of either compound against concentration of Eu(FOD)$_3$ is linear over the range studied, except for a slight curvature at very low relative concentrations of shift reagent. This behaviour has been noted before[12]. Least squares gradients of these lines are quoted in Table 2.

It is obvious from Table 2 that the two alcohols (VIA) and (VIB) are distinguishable by their behaviour with the shift reagent. The quoted gradients may be taken as a measure of the extent to which any given proton is affected by the lanthanide complex, and are therefore indicative of the geometry of the proton with

TABLE 1

CHEMICAL SHIFTS AND COUPLING CONSTANTS[a] FOR COMPOUNDS (VIA) AND (VIB) IN $CDCl_3$ SOLUTION

Proton	*Chemical shift* $(\nu_0\delta)^b$	
	(*VIA*)	(*VIB*)
H(1)	227.8	217.3
H(2)	65.7	49.0
H(3)	317.0	310.0
H(4)	317.0	324.0
H(5)	103.0	108.4
H(5')	17.0	23.8
Me	81.5	81.2
$J_{1,2}=6.5$*	$J_{1,3}\approx 0.0$	$J_{5,5'}=3.0$
$J_{2,3}=8.7$*	$J_{2,4}=1.0$	
$J_{3,4}=4.5$*	$J_{3,5}=1.2$*	
$J_{4,5}=7.0$*	$J_{3,5'}=1.0$*	
$J_{4,5'}=9.0$*		
$J_{1,Me}=6.5$*		



[a] Couplings are quoted in Hz, those marked with an asterisk were verified by spin-decoupling a suitable *shifted* spectrum. The values apply equally to (VIA) and (VIB) within the estimated error limits (±0.3 Hz).
[b] $\nu_0=60.004$ MHz.

respect to the lanthanide metal atom. For H(1) and the methyl group protons, which have the same spatial co-ordinates with respect to the metal in both (VIA) and (VIB), the greater slopes recorded for these protons in the former alcohol suggest that (VIA) forms a stronger complex with $Eu(FOD)_3$ than does (VIB). The fact that the two diastereomers are distinguishable in this way indicates that the two alcohols do in fact have preferred conformations since free rotation about the C(2)–C(3) bond would average out such differences.

TABLE 2

LEAST SQUARES GRADIENTS[a] OF THE LINEAR PLOTS OF SHIFT *v.* CONCENTRATION OF $Eu(FOD)_3$ FOR COMPOUNDS (VIA) AND (VIB)

Proton	*Compound*	
	(*VIA*)	(*VIB*)
H(1)	0.284	0.192
H(2)	0.164	0.136
H(3)	0.158	0.081
H(4)	0.043	0.021
H(5)	0.039	0.023
H(5')	0.060	0.046
Me	0.186	0.113

[a] Units, though arbitrary, are the same for both compounds. Gradients were calculated from data for the shifted spectra only, the positions of the resonances in absence of shift reagent were not included.

Three other important differences are apparent from a consideration of Table 2.

(*i*). For compound (VIA) H(4) is affected to a greater extent than H(5), whilst for (VIB) this order is reversed.

(*ii*). Similarly, the methyl protons of (VIA) shift more than does H(2), this order is again reversed in (VIB).

(*iii*). For (VIA) the shifts of H(2) and H(3) are similar, whereas for (VIB) H(2) is shifted rather more than H(3).

Point (*iii*) is most readily interpreted in terms of the geometry of the alcohol. For H(2) and H(3) to have similar shifts it is necessary for the Eu atom to lie roughly equidistant from both protons. Adopting the conformations proposed by Clinton and Lillya[2] therefore suggests that (VIA) exists as the *ψ-exo* form. Using a model based on the dimensions quoted by these authors[2], and having C–H bond lengths of 1.00 Å for the butadiene fragment, a configuration was adopted for the *ψ-exo* species which predicts closely similar values for the shifts experienced by H(2) and H(3). Geometrical factors were then calculated for all protons of the complex based on this structure from eqn. (1), these values are quoted in Table 3. A similar process was applied to the *ψ-endo* configuration of the complex. The geometrical factors obtained in this way reflect fairly closely the behaviour of the corresponding protons on adding the shift reagent. It may be seen from eqn. (1) that a plot of the geometrical factor against the proton shift should be linear for any given compound. This holds fairly well for the alcohol (VIA) in the *ψ-exo* configuration, and for (VIB) in the *ψ-endo* configuration, but not for (VIB) in the *ψ-exo* form.

If the shift reagent analysis is correct, alcohol (VIA) has the *ψ-exo* configuration, and (VIB) the *ψ-endo* form, *i.e.* cation hydrolysis leads to the *RS* and *SR* racemate, rather than *RR* and *SS*. This assignment cannot be regarded as conclusive owing to

TABLE 3

GEOMETRICAL FACTORS [$\text{G.F.}=10^2\ (3\cos^2 X_i-1)\cdot R_i^{-3}$] FOR PROTONS OF (VIA) AND (VIB) IN THE *ψ-exo* AND *ψ-endo* CONFIGURATIONS

Proton	*R* (Å)	*X* (°)	($3\cos^2 X-1$)	*G.F.*
(*a*). *ψ-exo: calculated for Me–C(2)–C(3)–H(2) dihedral angle of* ≈12°, *an Eu–O bond length of* 3.0 Å, *and an Eu–O–C angle of* 120°				
H(1)	4.0	31	1.214	1.90
H(2)	5.6	21	1.616	0.92
H(3)	5.9	7	1.958	0.95
H(4)	7.9	6	1.970	0.40
H(5)	8.5	19	1.685	0.28
H(5′)	7.1	22	1.577	0.44
Me	4.4	38	0.863	1.01
(*b*). *ψ-endo: calculated for Me–C(2)–C(3)–H(2) dihedral angle of* ≈15°				
H(1)	4.0	31	1.214	1.90
H(2)	5.4	4	1.988	1.26
H(3)	6.6	24	1.502	0.52
H(4)	8.5	11	1.838	0.30
H(5)	8.8	3	1.994	0.29
H(5′)	7.1	7	1.940	0.54
Me	4.4	38	0.863	1.01

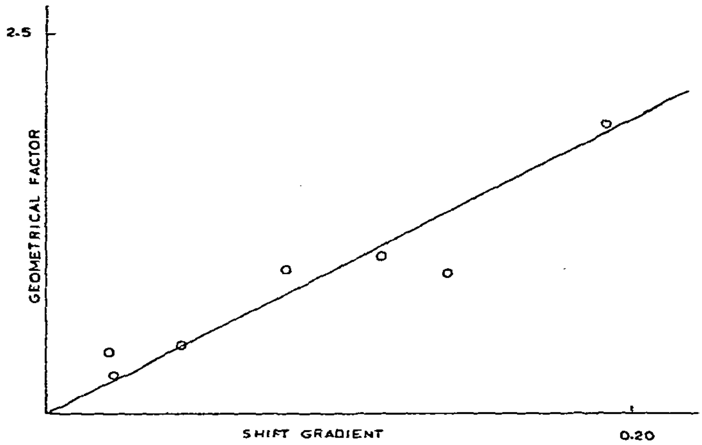
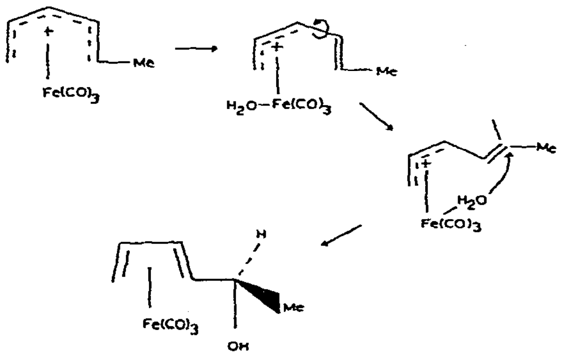


Fig. 1 (a). Plot of shift gradient for protons of (VIB) against geometrical factors appropriate to the ψ-*exo* configuration.

the number of approximations involved, particularly with regard to neglect of shifts due to contact interactions, which may arise through transfer of spin density through delocalised systems such as those discussed here. An X-ray crystallographic study is therefore currently being undertaken to resolve the matter finally. However, it is perhaps appropriate to speculate on mechanisms by which hydrolysis of the cation analogous to (I) could yield the *RS*, *SR* racemate. Two main possibilities seem likely:

(*i*). Attack by H_2O on the intermediate proposed by Pettit and Mahler[1] from the same side of the diene system as the iron tricarbonyl grouping. If the iron atom of the intermediate is indeed hydrated, the associated water molecule seems ideally placed for such attack.



(*ii*). Addition of H_2O directly to the cation to form a *cis*-alcohol, which then re-arranges to the *trans*-isomer. There is some precedent for such a rearrangement in that attempts to prepare *cis*-1,3-pentadieneiron tricarbonyl by reaction of *cis*-1,3-pentadiene with iron pentacarbonyl yield exclusively the *trans*-isomer[1].

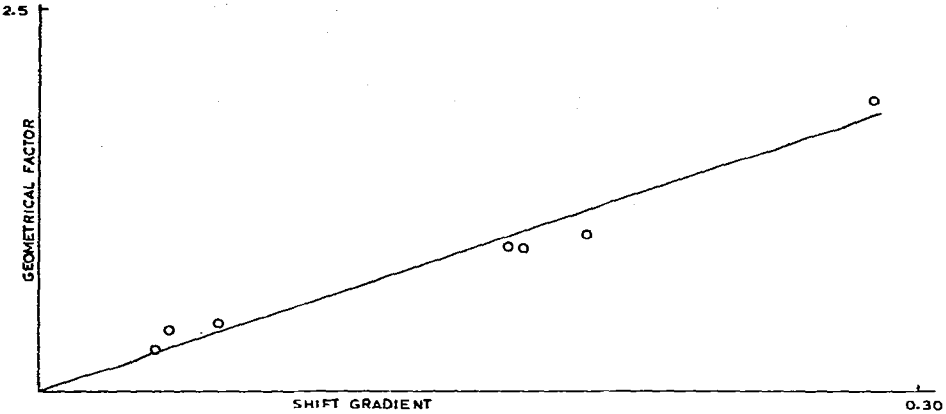


Fig. 1 (b). Plot of shift gradients of protons of (VIA) against geometrical factors appropriate to the ψ-*exo* configuration.

EXPERIMENTAL

NMR Spectra were obtained using a Perkin–Elmer R.10 spectrometer operating at 60.004 MHz. Line positions were determined relative to side-bands on internal TMS generated by a Muirhead D-880-A decade oscillator.

Spectra of the substrate in the presence of shift reagent were obtained in the following way: A stock solution of approximately 0.2 *M* (VIA) or (VIB) was made up in $CDCl_3$ previously purged with nitrogen. The "stock" solution was filtered through charcoal and divided into two halves, one half being saturated with $Eu(FOD)_3$, the remainder was transferred to a suitable NMR tube and the spectrum determined. To this sample was then added successive small aliquots of the $Eu(FOD)_3$ solution, the spectrum being re-run at each stage. This provided a convenient method of maintaining a constant concentration of the substrate material, the concentration of $Eu(FOD)_3$ being determined from the ligand integral as described in the text.

Anhydrous $Eu(FOD)_3$ was prepared by the method of Springer *et al.*[13] recrystallised twice from dichloromethane and stored under vacuum over P_2O_5. Proton shifts of up to 6 ppm (not including the $-OH$ resonance) were effected in the alcohols (VIA) and (VIB) using this reagent.

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