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DIENYL COMPLEXES OF TRANSITION METALS

VI *. THE ADDITION OF HYDRIDE TO (METHYL BENZOATE)CYCLOPENTADIENYLIRON CATION

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Summary

The addition of hydride to (methyl benzoate)cyclopentadienyliron cation occurs exclusively at the arene ring with reaction at the positions *ortho* to the ester group strongly favoured. Factors affecting the product distribution in nucleophilic addition reactions of arenecyclopentadienyliron cations are discussed in relation to the results obtained in this and earlier studies.

Introduction

Arenecyclopentadienyliron cations of type I undergo *exo* addition of nucleophiles (e.g. H^-, Me^-) exclusively at unsubstituted arene ring positions giving neutral (cyclohexadienyl)cyclopentadienyliron products [1]. In such reactions, the relative reactivities of the arene sites towards nucleophilic addition are influenced by the electronic character of the substituent X already present. Thus, a chloro substituent (cf. Ia) exerts an *ortho*-directing effect and the main product of addition of hydride, for example, is the 1-chlorocyclohexadienyl complex IIa [1b]. The anisole cation Ib, on the other hand, undergoes hydride addition predominantly at the *meta* positions giving the 2-methoxy product IIIb [1c] while the *ortho*, *meta*, and *para* positions of the toluene complex Ic are equally reactive towards hydride and the products IIc, IIIc, and IVc are formed in statistical proportions (2 : 2 : 1 respectively) [1a].

Having studied the influence in these reactions of arene substituents exerting (+*I*) and (—*I* + *R*) electronic effects, we have now extended the investigation to a (—*I* — *R*) group and in this paper we report the results of hydride addition to the cationic methyl benzoate complex Id.

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* For part V, see ref. 1e.

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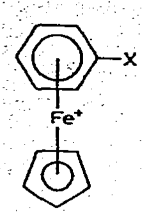
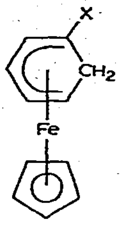


(I)



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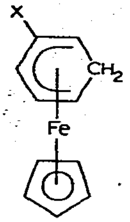

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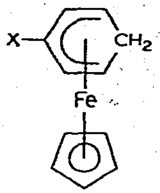

(IV)

a; X = Cl
b; X = OMe
c; X = Me
d; X = CO_2Me
e; X = CO_2H

Results and discussion

The hexafluorophosphate salt of (benzoic acid) cyclopentadienyliron cation (Ie), which was prepared according to the method of Nesmeyanov et al. [2] by permanganate oxidation of the toluene complex Ic, was converted to the ester Id; PF_6^- by treatment with dimethyl sulphate in refluxing methanol solution. This ester reacted cleanly with $NaBH_4$ in 1,2-dimethoxyethane to give a high yield of a viscous deep red oil which was separated into two bands by chromatography on alumina. By means of ^1H NMR spectroscopy (vide infra), it was found that the major and more polar of these bands contained solely the 1-(methoxycarbonyl)cyclohexadienyl complex IId while the minor band yielded a mixture of the 2- (IIId) and 3-methoxycarbonyl (IVd) isomers. These minor products could not be separated completely by rechromatography but samples containing a preponderance of each were obtained by a procedure of "topping and tailing" the chromatographic band and the ^1H NMR resonances associated with each isomer were thereby identified. These esters underwent hydride abstraction on treatment with trityl tetrafluoroborate giving a quantitative yield of the salt (Id; BF_4^-).

The ^1H NMR spectra of the three ester products, which are summarised in Table 1, exhibit many of the features established previously for complexes of types II—IV and the structural assignments are securely based. In particular, the resonance patterns for the cyclohexadienyl protons in each spectrum are distinctive and the enhanced deshielding of the methyl protons of the 3-CO_2Me isomer IVd accords with previous experience [1].

Careful analysis of the product mixtures from several experiments established that the esters IId—IVd are the sole products of hydride reduction of the cation Id. The relative proportions of these products were calculated from the weights of material contained in the major (i.e. IId) and minor (i.e. IIId + IVd) chromatographic bands and from the integrated relative areas of the singlet methoxyl resonances at τ 6.07 ppm (IVd) and 6.31 ppm (IIId) in the spectrum of the total product from the minor band. Good consistency was found in the results of several such analyses and the averaged values obtained for the product composition were 89% (IId), 7% (IIId), and 4% (IVd). Applying a correction for a statistical factor (two *ortho*, two *meta*, but one *para* position in the precursor), the relative arene site reactivities in the reaction are therefore found to be *ortho* :

TABLE 1

^{1}H NMR SPECTRA OF ESTERS [a]

Ester	Proton resonances [b]		
	C_5H_5 [c]	CO_2Me [c]	cyclohexadienyl [d]
IId	5.74	6.30	3.65 [td; H(3)] 4.70 [dt; H(2)] 5.40 [m; H(4)] 6.9—7.6 [m; H(5) + H(6-*endo*)] 8.70 [d; H(6-*exo*)]
IIId	5.78	6.31	3.10 [bd; H(3)] 5.63 [bt; H(4)] 7.0—8.0 [m; H(1) + H(5) + H(6-*endo*)] 8.5—8.9 [m; H(6-*exo*)]
IVd	5.80	6.07	4.85 [d; H(2) + H(4)] 7.0—8.0 [m; H(1) + H(5) + H(6-*endo*)] 8.5—8.9 [m; H(6-*exo*)]

[a] For $CDCl_3$ solutions with TMS as internal standard. [b] τ-Values; (td) triplet of doublets, (dt) doublet of triplets, (m) multiplet, (d) doublet, (bd) broadened doublet, (bt) broadened triplet. [c] Singlet resonances. [d] Coupling constants fell in the ranges previously found for other cyclohexadienyl complexes (see ref. 1c).

meta : *para* = 12.7 : 1.0 : 1.1, i.e. the carbons *ortho* to the ester function in the cation Id are approximately thirteen times more reactive towards addition of hydride than the corresponding *meta* and *para* carbons which have a similar reactivity.

From results now available, an assessment can be made of the effect of the arene substituent X upon the course of nucleophilic addition reactions of complexes of type I *. The variations in the arene site reactivities (see Table 2) suggest that product distribution is controlled principally by differences in positive charge concentration at the various arene carbons occasioned by the presence of the ring substituent. Assuming that the transition states for reaction are substrate-like, increase in positive charge at a particular site would be expected to facilitate addition of a nucleophile. Accordingly, electron-withdrawing substituents (e.g. X = Cl and CO_2Me) act to increase the local positive charge at the *ortho* relative

TABLE 2

SITE REACTIVITIES FOR HYDRIDE ADDITION REACTIONS OF ARENECYCLOPENTADIENYLIRON CATIONS

Cation	X	Electronic effect	Relative arene site reactivity [a]			Reference
			ortho	*meta*	*para*	
Ia	Cl	$-I > +R$	4	1	0 [b]	1b
Ib	OMe	$-I < +R$	0.2	1	0.6	1c
Ic	Me	$+I$	1	1	1	1a
Id	CO_2Me	$-I - R$	12.7	1	1.1	this study

[a] The *meta*-position is assigned unit reactivity in each case. [b] No product of addition to the *para*-position was detected.

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* Similar directing effects have been found for nucleophilic addition reactions of arenetricarbonylmanganese cations (see ref. 3).

to the *meta* and *para* positions and thereby favour the formation of products of type II. Although inductive (or hyperconjugative) electron donation has no discernible discriminatory influence upon product formation (cf. X = Me), the *meta*-directing property of the methoxyl group points to the importance of a (+R) effect by which the positive charge concentration at the *ortho* and *para* positions of the cation Ib is reduced through mesomeric donation of p-electron density from the oxygen atom [1c]. It is noteworthy that, whereas the *para* position of the chlorobenzene complex Ia is inert towards nucleophilic addition [1b] (+R effect of Cl?), the *para* position of the methyl benzoate complex Id is at least as reactive towards hydride addition as the *meta* position. This may reflect some activation of the *para* carbon through operation of the (—R) effect of the CO_2Me group although this effect is felt much more strongly by the *ortho* carbons.

Experimental

All reactions were carried out under an atmosphere of pure, dry N_2. Chromatography was carried out using neutral alumina which was prepared by storing Spence Grade H alumina under EtOAc for several days, then washing with MeOH then H_2O, and drying at 160°C for 5 h. Light petroleum refers to the fraction of b.p. 40—60°C. ^1H NMR spectra were recorded on a Perkin—Elmer R12A spectrometer operating at 60 MHz. Microanalyses were performed by the Alfred Bernhardt Microanalytical Laboratory, Mulheim, West Germany.

(Methyl benzoate)cyclopentadienyliron salts (Id; PF_6^-, Id; BF_4^-)

(a) Freshly distilled dimethyl sulphate (5.0 g; 40 mmol) was added in portions over 3 h to a refluxing solution of (benzoic acid)cyclopentadienyliron hexafluorophosphate [2] (9.7 g; 25 mmol) in anhydrous MeOH (50 ml). During the reaction, sufficient KOH in anhydrous MeOH was added periodically to keep the solution just acid. The mixture was refluxed overnight, then cooled, and the precipitated K_2SO_4 was filtered off. The filtrate was poured into ether giving the salt (Id; PF_6^-) (6.25 g; 62%), a bright yellow solid, which was purified by recrystallisation from acetone/ether; τ (CD_3COCD_3) (ppm) 2.7—3.4 (5H, m, Ph), 4.63 (5H, s, C_5H_5), and 6.38 (3H, s, OMe).

(b) A solution of the ester IId (85 mg; 0.33 mmol) in CH_2Cl_2 (2 ml) was added to a solution of trityl tetrafluoroborate (110 mg; 0.33 mmol) in CH_2Cl_2 (2 ml). The clear pale yellow solution was diluted with ether giving a precipitate of the salt (Id; BF_4^-) (102 mg; 90%), a yellow solid, m.p. 134—136°C (Found: C, 45.7; H, 3.9. $C_{13}H_{13}BF_4FeO_2$ calcd. C, 45.4; H, 3.8%). The ^1H NMR spectrum of this salt in CD_3COCD_3 was identical with that of the PF_6^- salt given above.

Hydride reduction of salt (Id; PF_6^-)

$NaBH_4$ (1 g) was added in portions to a stirred solution of the salt (Id; PF_6^-) (4.0 g; 10 mmol) in 1,2-dimethoxyethane (50 ml). The mixture, which quickly became red, was stirred overnight and then poured into water (200 ml) and extracted thoroughly with ether. The extract was washed (H_2O), dried ($MgSO_4$), and evaporated. The residual viscous oil was dissolved in light petroleum and chromatographed. Light petroleum/ether (9/1) eluted two red bands which were clearly separated. The less polar band afforded a mixture of the esters IIId and IVd (245 mg; 10%), a viscous red oil (Found: C, 60.7; H, 5.5. $C_{13}H_{14}FeO_2$ calcd.

C, 60.5; H, 5.5%). The second band afforded the ester IId (1.98 g; 81%), a viscous red oil (Found: C, 60.6; H, 5.6. $C_{13}H_{14}FeO_2$ calcd. C, 60.5; H, 5.5%).

The mixture of esters IIId + IVd was rechromatographed on a long thin column using light petroleum/ether (20/1) as eluant. From the forerunnings and tailings of the band, a fraction enriched (ca. 80%) in each isomer was obtained. The ^{1}H NMR resonances of these products, which were not completely separated, are given in Table 1 together with those of the isomer IId.

Determination of product composition

From several independent experiments, which gave reproducible results, the product ratio IId : IIId + IVd was calculated from the weights of material contained in the aforementioned chromatographic bands and found to be 89 : 11. From the ^{1}H NMR spectra of the total material from the less polar band from these experiments, integration of the methoxyl resonances at τ 6.07 and 6.31 ppm gave the product ratio IVd : IIId as 4 : 7 (average of several determinations). The ratio of products formed in the hydride reduction of the cation Id was therefore found to be IId : IIId : IVd = 89 : 7 : 4.

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