The Transmission of Electronic Effects in Ferrocene

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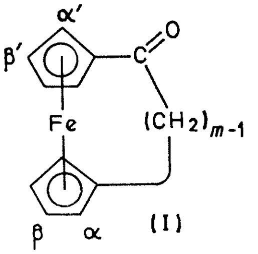
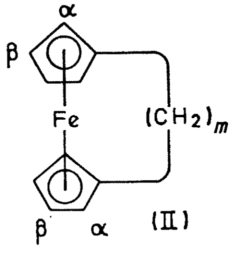
Summary The directive influence of a carbonyl group upon the electrophilic substitution of ferrocene has been investigated through study of the Friedel–Crafts acetylation of a series of [*m*]ferrocenophan-1-ones.

THE mechanism by which electronic effects are transmitted in ferrocene has been a subject of speculation and controversy.[1] From a number of observations, it is clear that electronic perturbation of one ring in the molecule by a substituent is transmitted not only to the iron atom but also, to a diminished extent, to the other ring although the nature of the interactions involved is poorly understood. In an attempt to clarify the situation, we have investigated the directive influence of a carbonyl group in Friedel–Crafts acetylation reactions of a series of [*m*]ferrocenophan-1-ones (I; $m = 3$, 4, and 5). These substrates were chosen because of their unique conformational properties[2] which permit variation of the relative torsional freedom of the cyclopentadienyl rings and of the orientation of the carbonyl group with respect to the ferrocene nucleus.



(I)



(II)

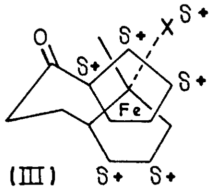
Isomer ratios in acetylation reactions[a]

Bridge length (m)	Ketones (I) α'/α	Ketones (I) β/α	Ferrocenophanes (II)[b] β/α
3	0·5—0·6	4·1—4·2	1·57
4	0·45—0·55	1·1—1·3	1·65
5	0·006—0·01	0·7—0·8	2·19

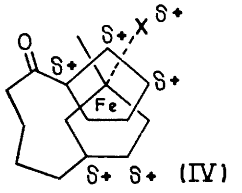
[a] Positions are designated in formulae in text.
[b] Ref. 4.

The acetylation reactions were conducted in methylene chloride solution under standard conditions using acetyl chloride and aluminium chloride. At least two separate runs were carried out for each substrate and reproducible results were obtained. Separation of pure samples of the various isomeric products was achieved by chromatography on alumina. The structures of these acetyl[*m*]ferrocenophan-1-ones were unambiguously established by analytical and spectroscopic techniques and by their conversion into compounds of known structure. Details of these correlations are deferred to a full paper. Analysis of product composition was carried out by chromatographic separation and by ^{1}H n.m.r. spectroscopy. Fortuitously, the chemical shifts of the acetyl proton singlets in the spectra of isomers of a series were sufficiently separated to permit analysis of mixtures by integration of these signals.[3] The combined yields of products were high (70—98%) and no diacetyl derivatives were detected. The results of these experiments are summarised in the Table together with those previously obtained[4] for the acetylation of the corresponding [*m*]ferrocenophanes (II; $m = 3$, 4, and 5). They are presented as isomer ratios relative to the proportion of the α-acetyl products (see formulae for positional labels).

Several conclusions emerge from this study. Considering the carbonyl-substituted ring of the ketones (I), α′-substitution is favoured to the extent that no β′-acetyl derivatives were detected. In the case of the [5]-ketone (I; $m = 5$), however, the longer bridge length permits attainment by the carbonyl group of coplanarity with the ring[2] which, overall, is thereby deactivated towards electrophilic attack and the reactivity of the α′-positions is greatly reduced. This deactivation is therefore established as a predominantly resonance (—*R*) interaction between the ring and the attached group.† The results further suggest that, in the transition state for addition of an electrophile to a ring in ferrocene, a greater proportion of positive charge accumulates at positions β to the substitution site.‡ Consequently, reaction at the position (α′) adjacent to the carbonyl group in the ketones (I) is preferred (*cf.* theoretical prediction[6]).



(III)



(IV)

The most interesting feature of the results is the remarkable sensitivity of the substitution pattern in the alkyl-substituted ring to the interannular bridge length. In the case of the [3]-ketone (I; $m = 3$), substitution at the β-positions is favoured by a much greater factor than that found for the corresponding ferrocenophane (II; $m = 3$) (see Table). Since steric shielding of the α-positions by the bridges in each of these compounds should be of a similar magnitude, an interannular directive influence by the bridge carbonyl group is clearly demanded. Although field effects may be important, it can be argued that, in the transition state for electrophilic addition to a ring in ferrocene, the accumulation of positive charge at positions β to the substitution site (*vide supra*) produces a sympathetic polarisation of the bonds disposed from the iron atom to carbon atoms pseudo-*trans* to these electron-deficient centres. By this mechanism, positive charge is thus transmitted stereospecifically between the rings.

With non-bridged substrates, in which free relative

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† In the reaction medium, the bridge carbonyl group is present as a Lewis complex with the aluminium chloride.

‡ A similar electronic situation may obtain with the closely analogous ferrocenylcarbonium ions ($\mathrm{Fc\overset{+}{C}R_2}$) whose β-ring protons, for example, resonate at much lower field than the corresponding α-protons.[5]

rotation of the rings is possible, the operation of such an interannular electronic effect cannot be investigated. The relative torsion of the rings in the [3]-ketone (I; $m = 3$), however, is greatly restricted.[2] Addition of an electrophile (X^+) to a ring position α to the alkyl substituent would produce a relatively unfavourable development of positive charge at the carbonyl-substituted position in the other ring (see III) and β-substitution is consequently favoured.

Despite the operation of steric effects which favour β-substitution, particularly in the [5]-system [*cf.* β/α ratios for the corresponding ferrocenophanes (II)], the relative reactivities of the α- and β-positions of the [4]- and [5]-ketones (I; $m = 4$ and 5, respectively) are similar in magnitude. In these systems, therefore, it appears that the bridge carbonyl group exerts a stereospecific deactivating effect upon the β-positions. This can be accounted for by a mechanism similar to that previously suggested for the [3]-ketone since the much greater torsional freedom of the rings[2] permits these molecules to adopt preferred conformations in which β-substitution is disfavoured (*e.g.* see IV).

Further research is designed to extend and evaluate these suggestions in relation to the various hypotheses[1,7] concerning the mechanism of electrophilic substitution of ferrocene.

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[1] See M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Part I, Interscience, New York, 1965.

[2] T. H. Barr and W. E. Watts, *Tetrahedron*, 1968, **24**, 6111.

[3] *Cf.* K. Schlögl, H. Falk, and G. Haller, *Monatsh.*, 1967, **98**, 82.

[4] T. H. Barr, E. S. Bolton, H. L. Lentzner, and W. E. Watts, *Tetrahedron*, 1969, **25**, 5245.

[5] See W. M. Horspool and R. G. Sutherland, *Chem. Comm.*, 1967, 786.

[6] J. H. Richards and T. J. Curphey, *Chem. and Ind.*, 1956, 1456; M. Rosenblum and W. G. Howells, *J. Amer. Chem. Soc.*, 1962, **84**, 1167.

[7] See T. G. Traylor and J. C. Ware, *J. Amer. Chem. Soc.*, 1967, **89**, 2304; J. Feinberg and M. Rosenblum, *ibid.*, 1969, **91**, 4324.