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The relative thermodynamic stabilities of ferrocenylvinyl and -styryl systems

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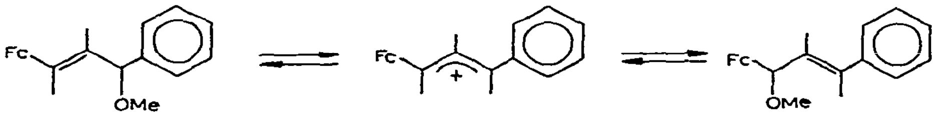
We have previously shown[1] that, in the 1-ferrocenyl-3-phenylallyl cation (I), positive charge is localised mainly on the carbon atom adjacent to the ferrocenyl group. In consequence, the reaction of this cation with methoxide anion under conditions of kinetic control affords a mixture of the isomeric ferrocenylvinyl and -styryl ethers (II and III respectively) in which the latter greatly predominates (*ca.* 88% of the mixture). In this connection, we wished to establish the relative thermodynamic stabilities of these allyl ethers such that a direct comparison between the conjugative powers of ferrocenyl and phenyl groups towards an ethylenic bond could be obtained.



(II) (I) (III)

Treatment of either ether (II or III) in methanol solution with a trace of aqueous sulphuric acid (1 drop 0.5*M* acid per 100 ml solution) promotes very fast equilibration to produce the same isomeric mixture whose composition was unchanged with time. Since the concentration of the intermediate cation (I) in these solutions was insignificant*, analysis of the mixture could be conveniently achieved by ultraviolet spectroscopy[2] which established that the ferrocenylvinyl isomer (II) predominates at equilibrium (60 ± 2% of the mixture). Assuming that hyperconjugative interactions between the ethylenic system and the groups attached to the allylic carbon atom provide a relatively insignificant contribution to the stability of these compounds, the derived free energy change (ΔG = *ca.* 1.2 kJ/mole) represents the difference between the conjugation energies of an ethylenic bond with a ferrocenyl and a phenyl group. The interaction of the former confers the greater thermodynamic stability.

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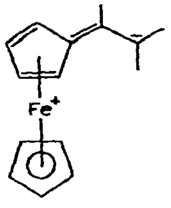
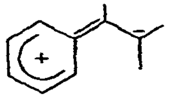
*The cation (I), which is formed quantitatively from either ether (II or III) in strong acids (*e.g.* conc. HCl, 50% H_2SO_4 aq., CF_3CO_2H), has a characteristic electronic spectrum which is quite distinct from those of the precursors.



(IV)



(V)

It may be concluded from this result that the contribution of the dipolar resonance form (IV) to the structure of alkenylferrocenes is relatively more important than that of structure (V) in the styryl analogues. In the latter case, polarisation in the direction indicated has been established by a study of substituent effects in the equilibration reaction. Thus, the styryl system in the ether (III) is destabilised by the presence of groups exerting a negative inductive effect (*e.g.* *m*-OCH_3). The preponderance of the corresponding ferrocenylvinyl isomer in the equilibrium mixture is thereby increased (70 ± 2% in the *m*-OCH_3 example). In agreement with the conclusions from previous work[3], it was found that the extra-conjugative stabilisation provided by a *p*-methoxyl substituent in the styryl system is minimal. The relative proportions of the ferrocenylvinyl and -anisyl ethers in this equilibrium mixture were very similar to those found for the unsubstituted analogues.

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3 S.C. Bernstein. *J. Org. Chem.*, 33 (1968) 3486.