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Preliminary communication

THE PROPERTIES OF FERROCENYLVINYL CATIONS IN SOLUTION: INTER- AND INTRA-MOLECULAR TRAPPING

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Summary

Ferrocenylvinyl cations have been generated in solution from alkynylferrocene precursors and their reactions have been investigated.

We recently reported [1] that direct PMR spectroscopic observation of ferrocenylvinyl cations (II) in CF_3CO_2H solution is possible[*] when the reactive α-carbon atom is sterically shielded to nucleophilic attack by an adjacent bulky 2-alkyl ring substituent (e.g. IIa). Such vinyl cations collapse quickly, however, giving the more stable trifluoroacetoxycarbenium ions (III) by addition of a solvent molecule. We have since discovered that the presence of a bulky *exo*-alkyl group attached to the β-vinyl carbon atom provides much more effective steric shielding of the reactive centre, leading to much extended lifetimes of cations of this type.

Thus, protonation of t-butylethynylferrocene[**] (Ib) generated the vinyl cation (IIb), identified by PMR spectroscopy (singlet vinyl proton resonance at τ3.61), which was converted relatively slowly in CF_3CO_2H to the addition product IIIb. At 33°, the half-life of IIb was approximately 2 h. The importance of steric rather than electronic factors in determining the rate of collapse of ferrocenylvinyl cations is illustrated by the much shorter lifetime of the β-methyl-substituted cation (IIc), obtained by protonation of propynylferrocene (Ic). In CF_3CO_2H solution, only the PMR spectrum of the product IIIc of solvent capture was observed. The di-t-butyl-substituted alkyne (Id), on the other hand, dissolved in CF_3CO_2H to give a mixture of the two stereoisomeric forms (β-methyl group *exo* or *endo*) of the cation IId whose PMR resonances (doublet methyl resonances at τ7.64 and 7.68; quartet vinyl resonances at τ2.95 and 3.75; J = ca. 7 Hz) were only slowly replaced by

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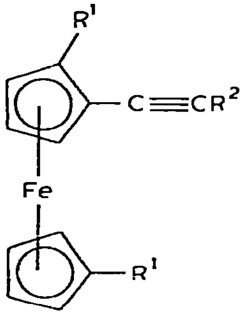
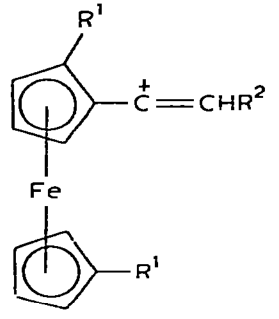
[*] PMR spectroscopic observation of an arylvinyl cation has recently been described [2].

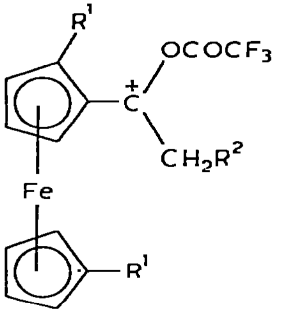
[**] This compound and the other alkynes used in this study were prepared by standard procedures and were satisfactorily characterised by analytical and spectroscopic methods.



(I)



(II)

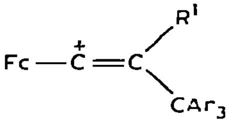


(III)

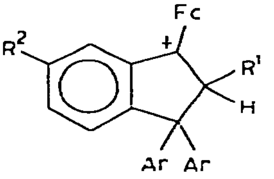
(a) R^1 = t-Bu ; R^2 = H
(b) R^1 = H, R^2 = t-Bu
(c) R^1 = H ; R^2 = Me

(a) R^1 = t-Bu ; R^2 = Me
(e) R^1 = R^2 = H
(f) R^1 = H ; R^2 = CPh_3

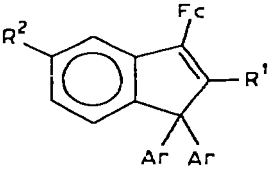
those of the addition product IIId. From these and other experiments, it is apparent that the stability of these ferrocenylvinyl cations towards capture by CF_3CO_2H increases through the series: IIe $\leqslant$ IIc $<$ IIa $<$ IId $<$ IIb.



(IV)



(V)



(VI)

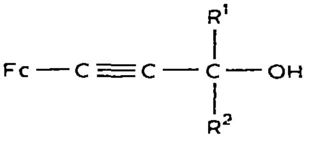
(a) R^1 = R^2 = H ; Ar = Ph
(b) R^1 = Me, R^2 = H ; Ar = Ph
(c) R^1 = H ; R^2 = Me ; Ar = C_6H_4Me-*p*

In an attempt to provide still more effective shielding of the reactive α-carbon atom of the system II, the β-trityl-substituted alkyne If was protonated in CF_3CO_2H solution. The PMR spectrum of this solution, however, showed no evidence for the presence of the expected vinyl cation IIf ($\equiv$ IVa) but instead corresponded to the tertiary carbenium ion Va. When this solution was quenched with Na_2CO_3 aq., the indene derivative VIa was formed in good yield. The PMR spectrum of VIa in CF_3CO_2H was identical with that of the cation derived by protonation of If.

The compound VIa could also be prepared by treatment of ethynylferrocene Ia with trityl tetrafluoroborate in CH_2Cl_2 solution followed by quenching with Na_2CO_3 aq. The alkyne Ic was likewise converted to the indene derivative VIb while similar treatment of ethynylferrocene (Ie) with tri-*p*-tolylmethyl tetrafluoroborate afforded the product VIc. The structures of these indenes and the related carbenium ions were established from their characteristic PMR spectra. For example, the spectrum of VIc in $CDCl_3$

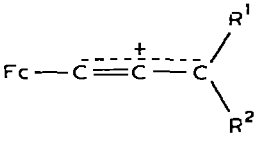
solution contained two methyl singlets at τ7.54 (3H) and 7.73 (6H) while that of the derived cation Vc in CF_3CO_2H solution showed three equally intense methyl singlets at τ7.49, 7.60, and 7.73. In the latter case, restricted rotation around the Fc—C$^+$ bond [3] renders non-equivalent the *p*-methyl groups of the two tolyl substituents in the five-membered ring.

These experiments show that the β-(triarylmethyl)vinyl cations (IV) formed either by alkyne protonation (e.g. from If) or by addition of Ar_3C^+ to alkynylferrocenes, readily undergo an internal electrophilic substitution reaction in which the electron-deficient vinyl α-carbon atom adds to an adjacent aryl ring to give, after deprotonation, indene derivatives of the type VI. In acidic media, these are reprotonated to give the corresponding carbenium ions V.

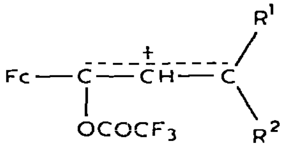


$Fc-C\equiv C-C(R^1)(R^2)-OH$

(VII)



(VIII)



(IX)

(a) $R^1 = R^2 = Me$

(b) $R^1 = Me; R^2 = Fc$

Finally, we have also investigated the properties of the mesomeric allenylic $\leftrightarrow$ propargylic cations (VIII) [4], obtained by dissolution of the acetylenic alcohols (VII) in CF_3CO_2H. We have found that these cations undergo fast addition of a solvent molecule to give the more stable trifluoroacetoxyallylic cations (IX). When these solutions are quenched with Na_2CO_3 aq., the corresponding α,β-unsaturated acylferrocenes FcCOCH=CMe$_2$ (from IXa) and FcCOCH=CMeFc (from IXb) may be isolated in good yield.

References

1 T.S. Abram and W.E. Watts, J. Chem Soc. Chem. Commun., (1974) 857
2 H.-U. Siehl, J.C. Carnahan, L. Eckes and M. Hanack, Angew. Chem. Intern. Edn., 13 (1974) 675.
3 T.D. Turbitt and W.E. Watts, J. Chem. Soc. Perkin II, (1974) 177
4 Cf. G.A. Olah, R.J. Spear, P.W. Westerman and J.-M. Denis, J. Amer. Chem. Soc., 96 (1974) 5855.