

## NOTE

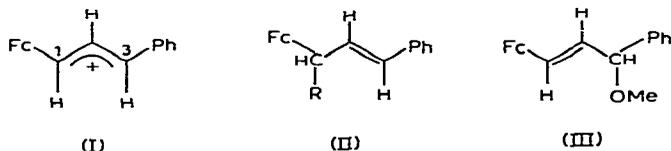
### CHARGE DISTRIBUTION IN THE 1-FERROCENYL-3-PHENYLALLYL CATION

M. J. A. HABIB AND W. E. WATTS

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow (Scotland)

(Received May 9th, 1969)

From a large accumulation of experimental data, it is clear that the ferrocenyl group (Fc) constitutes one of the most powerfully electron-releasing aromatic nuclei known<sup>1</sup>. In particular, it has been convincingly established<sup>2</sup> that ferrocenylcarbonium ions possess a remarkable stability which, in several instances, has permitted their isolation as stable salts<sup>3</sup>. The source of the stabilising influence is still in dispute<sup>2,4</sup>. The interaction of a ferrocenyl group with a mesomeric carbonium-ion system has not yet been studied and, in this connection, we wish to report results concerning the distribution of positive charge in the 1-ferrocenyl-3-phenylallyl cation (I).



The cation (I) is formed immediately and quantitatively on treatment of *trans*-3-ferrocenyl-1-phenylpropene [(II), R=H] in methylene chloride with an equimolar amount of triphenylmethyl tetrafluoroborate. An equivalent amount of triphenylmethane is formed in the reaction and the success of the hydride transfer implies that the cation (I) possesses significantly greater thermodynamic stability than the triphenylmethyl cation.

The precursor [(II), R=H] was prepared by mixed hydride ( $\text{LiAlH}_4/\text{AlCl}_3$ ) reduction<sup>5</sup> of *trans*-cinnamoylferrocene<sup>6</sup> and the structure was confirmed spectroscopically (details in Experimental). In particular, the location of the double bond adjacent to the phenyl group was established by the presence in the UV spectrum of a styryl chromophore<sup>7</sup> (251 nm;  $\epsilon$  21,620) and by the lack of appreciable splitting of the cyclopentadienyl ring proton signal in the PMR spectrum\*.

The cation (I) could be precipitated as a brown air-sensitive tetrafluoroborate salt by dilution of the aforementioned methylene chloride solution with ether.

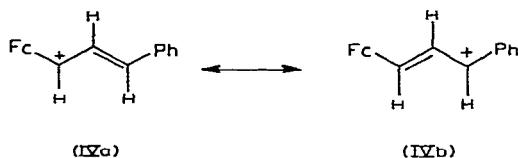
\* In the PMR spectra of alkenylferrocenes ( $\text{FcCH}=\text{CHR}$ ), the protons of the substituted cyclopentadienyl ring appear as an  $\text{A}_2\text{B}_2$  pattern comprising two triplets<sup>8</sup>.

Alternatively, on addition of sodium methoxide in methanol, an almost quantitative yield of a mixture of the ethers [(II), R = OMe] and (III) was isolated. These isomers were separated with some difficulty by chromatography and their structures were assigned from their spectral characteristics. The presence of a *trans*-substituted double bond in each compound was apparent from the magnitude (*ca.* 16 Hz) of the vinylic coupling constants in the PMR spectra while the UV spectra established the presence of a styryl group<sup>7</sup> in the former (253 nm;  $\epsilon$  19,500) and a ferrocenylvinyl group<sup>9</sup> in the latter (281 nm;  $\epsilon$  10,220).

Analysis of the UV spectrum of the total ether product from several such reactions showed that the isomers [(II), R = OMe] and (III) were formed from the cation (I) in consistent relative proportions, the former predominating ( $88 \pm 5\%$  of the mixture). Since it was shown in separate experiments that these ethers do not isomerise in the presence of methoxide under the original reaction conditions, the relative proportions formed result from a kinetically controlled reaction of the cation (I) with methoxide anion.

As pointed out<sup>10</sup> by Streitwieser *inter al.*, reactions between carbonium ions and Lewis bases should occur preferentially at the site of lowest electron density in the ion, in the absence of overriding steric effects. The relative proportions of isomers resulting from capture of the cation (I) under kinetically controlled conditions, therefore, should reflect the relative distribution of positive charge to the 1- and 3-positions.

Since it may be assumed that, in this situation, differences in steric shielding at the 1- and 3-positions are of secondary importance only, it may be concluded that



positive charge in the cation (I) is localised mainly on the carbon atom adjacent to the ferrocenyl group. In resonance terms, the contribution of structure (IVa) to the mesomeric cation is much more significant than that of structure (IVb).

#### EXPERIMENTAL

All reactions were carried out under an atmosphere of nitrogen. PMR spectra were obtained for deuteriochloroform solutions using a Perkin-Elmer R10 spectrometer. UV spectra were recorded on a Unicam SP800A spectrometer for absolute ethanol solutions and IR spectra on a Perkin-Elmer 257 spectrometer for potassium chloride discs. Chromatographies were carried out using Spence Grade H alumina which had been partially deactivated by exposure to the atmosphere for the periods indicated.

#### *trans*-3-Ferrocenyl-1-phenylpropene [(II), R = H]

*trans*-Cinnamoylferrocene<sup>6</sup> (10 g) was added portionwise to a stirred suspension of lithium aluminium hydride (1.4 g) and aluminium chloride (10 g) in ether (100 ml). The mixture was stirred overnight and then poured into ice/water. The ether layer

was separated and combined with several ether extracts of the aqueous phase. The total extract was dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated, and the residue was dissolved in light petroleum (40–60°) and chromatographed on alumina (6 h exposed). The same solvent eluted *trans*-3-ferrocenyl-1-phenylpropene (6.55 g; 69%) which crystallised from light petroleum as a yellow solid, m.p. 80.5–82°. (Found: C, 75.5; H, 6.2.  $\text{C}_{19}\text{H}_{18}\text{Fe}$  calcd.: C, 75.5; H, 6.0%.) UV 251 nm ( $\epsilon$  21,620); IR 964  $\text{cm}^{-1}$  (vinylic CH deformation); PMR  $\tau$  2.7 (bs; 5 H; phenyl), 3.5–3.8 (m; 2 H; vinyl), 5.88 and 5.93 (2 s; 9 H; ferrocenyl), 6.7–6.9 (m; 2 H; methylene). Light petroleum/ether mixtures eluted two further products whose structures have not yet been elucidated.

#### *Hydride-abstraction reactions*

A solution of triphenylmethyl tetrafluoroborate<sup>11</sup> (1.2 g) in methylene chloride (50 ml) was added to a solution of *trans*-1-ferrocenyl-3-phenylpropene (1.0 g) in methylene chloride (100 ml). The dark brown solution, which was formed instantaneously, was stirred for 1 h and then a solution of sodium methoxide (from 0.2 g Na) in methanol (5 ml) was added, the colour immediately reverting to orange-yellow. The solution was diluted with water (300 ml) and the organic layer separated and combined with several methylene chloride extracts of the aqueous phase. The total extract was dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated, and the residue was dissolved in light petroleum and chromatographed on alumina (72 h exposed). The same solvent eluted a mixture of triphenylmethane (0.68 g; 90%), m.p. 91–92° (lit. 92°), and unchanged alkene (0.06 g; 6% recovery) which was separated by partitioning with aqueous ferric chloride solution. Light petroleum/ether (19/1) then eluted a diffuse orange tailing to yellow band. From the first runnings there was obtained 1-ferrocenyl-3-methoxy-3-phenylpropene (III) which, after several recrystallisations from light petroleum at –70°, had m.p. 91.5–93°. (Found: C, 72.4; H, 5.9.  $\text{C}_{20}\text{H}_{20}\text{FeO}$  calcd.: C, 72.3; H, 6.0%.) UV 281 nm ( $\epsilon$  10,220); IR 962  $\text{cm}^{-1}$  (vinylic CH deformation); PMR  $\tau$  2.63 (bs; 5 H; phenyl), 3.45–4.35 (AB portion of ABX pattern; 2 H; vinyl;  $J_{\text{AB}} \sim 16$  Hz,  $J_{\text{AX}} \sim 0$  Hz,  $J_{\text{BX}} \sim 7$  Hz), 5.30 (d; 1 H; methine), 5.65 and 5.82 (2 t; 4 H; cyclopentadienyl), 5.92 (s; 5 H; cyclopentadienyl), 6.62 (s; 3 H; methoxyl).

From the tailings of the same band there was obtained 3-ferrocenyl-3-methoxy-1-phenylpropene [(II), R = OMe] which, after several recrystallisations from light petroleum at –70°, had m.p. 53–55°. (Found: C, 72.6; H, 6.1.  $\text{C}_{20}\text{H}_{20}\text{FeO}$  calcd.: C, 72.3; H, 6.0%.) UV 253 nm ( $\epsilon$  19,500); IR 958  $\text{cm}^{-1}$  (vinylic CH deformation); PMR  $\tau$  2.4–2.8 (m; 5 H; phenyl), 3.1–3.8 (AB portion of ABX pattern; 2 H; vinyl;  $J_{\text{AB}} \sim 16$  Hz,  $J_{\text{AX}} \sim 0$  Hz,  $J_{\text{BX}} \sim 7$  Hz), 5.44 (d; 1 H; methine), 5.70–5.85 (m; 9 H; ferrocenyl), 6.64 (s; 3 H; methoxyl).

The experiment was repeated using identical quantities of reactants. The mixture of products was chromatographed on alumina (5 days exposed) and the total ether band was collected, affording a mixture of the isomeric ethers (0.93 g; 91%). The UV spectrum of this mixture was determined and the extinction coefficient at 253 nm calculated. From fine such experiments, it was estimated\* that the mixture contained  $88 \pm 5\%$  of the styryl ether [(II), R = OMe] and  $12 \pm 5\%$  of the isomer (III).

Treatment of either of these ethers in methylene chloride solution with sodium methoxide in methanol under the conditions of the original experiment gave back

\* The spectra of predetermined mixtures of these ethers showed excellent agreement with Beer's law.

unchanged starting material in quantitative amounts.

#### ACKNOWLEDGEMENT

We thank Mr. F. Daubney for microanalyses and Mr. J. Ritchie for PMR spectra.

#### REFERENCES

- 1 M. ROSENBLUM, *Chemistry of the Iron Group Metallocenes*, Part 1, Interscience, New York, 1965, p. 129 *et seq.*
  - 2 M. CAIS, *Organometal. Chem. Rev.*, 1 (1966) 435.
  - 3 *E.g.* M. CAIS AND A. EISENSTADT, *J. Org. Chem.*, 30 (1965) 1148; *J. Amer. Chem. Soc.*, 89 (1967) 5468; A. N. NESMEYANOV, V. A. SAZONOVA, G. I. ZUDKOVA AND L. S. ISAEVA, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1966) 2017.
  - 4 J. D. FITZPATRICK, L. WATTS AND R. PETTIT, *Tetrahedron Lett.*, (1966) 1299; T. G. TRAYLOR AND J. C. WARE, *J. Amer. Chem. Soc.*, 89 (1967) 2304; J. L. DANNENBERG AND J. H. RICHARDS, *Tetrahedron Lett.*, (1967) 4747; E. A. HILL AND R. WIESNER, *J. Amer. Chem. Soc.*, 91 (1969) 509.
  - 5 K. SCHLÖGL, A. MOHAR AND M. PETERLIK, *Monatsh. Chem.*, 92 (1961) 921.
  - 6 M. D. RAUSCH AND L. E. COLEMAN, *J. Org. Chem.*, 23 (1958) 107.
  - 7 A. E. GILLAM AND E. S. STERN, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*, Arnold, London, 1958, p. 254.
  - 8 W. M. HORSPOOL AND R. G. SUTHERLAND, *Can. J. Chem.*, 46 (1968) 3453.
  - 9 K. SCHLÖGL AND H. EGGER, *Justus Liebigs Ann. Chem.*, 676 (1964) 88.
  - 10 A. STREITWIESER, *Molecular Orbital Theory for Organic Chemists*, Wiley, New York, 1961, p. 378-379.
  - 11 H. J. DAUBEN, L. R. HONNEN AND K. M. HARMON, *J. Org. Chem.*, 25 (1960) 1442.
- J. Organometal. Chem.*, 18 (1969) 361-364