Journal of Organometallic Chemistry, 185 (1980) 443–447
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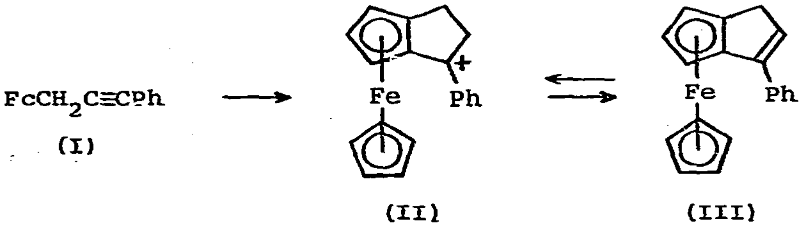
STABLE CARBOCATIONS. PART 21.† INTRA-IONIC PROTON TRANSFER IN ELECTROPHILIC CYCLISATION OF 3-FERROCENYL-1-PHENYLPROPEN-1-YL CATION

William Crawford and William E. Watts*
School of Physical Sciences, New University of Ulster, Coleraine
(Northern Ireland)

(Received October 31st, 1979)

Summary The spontaneous conversion of the title cation into the 1-phenyl[3](1,2)ferrocenophan-1-yl cation proceeds by intra-ionic 1,3-shift of a cyclopentadienyl α-ring proton to C(2) of the homoannular bridge; the latter cation undergoes deprotonation by stereospecific loss of the exo-proton adjacent to C^+.

In an earlier paper [2], we reported that the alkyne (I) undergoes cyclisation in CF_3CO_2H to the ferrocenophanyl cation (II) which can be reversibly deprotonated to the cycloalkene (III). In connection with a study [3] of the stereochemistry of such proton transfers, this reaction has been reinvestigated using deuterium-labelled substrates.



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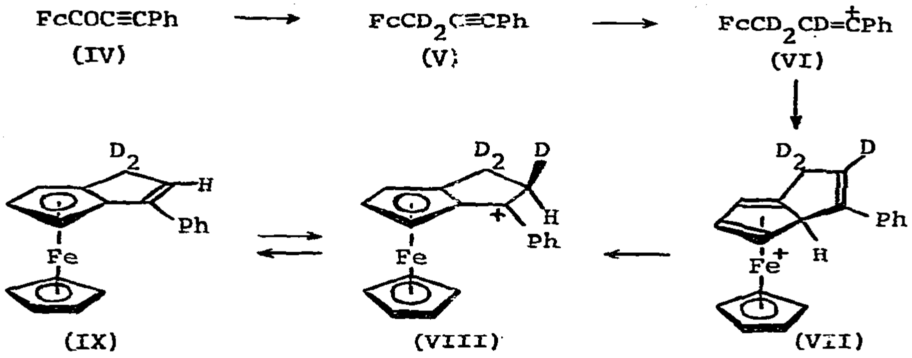
† For Part 20, see ref. 1.

SCHEME



Reduction of the ketone (IV) in ether with "mixed-deuteride" reagent ($LiAlD_4$-Al_2Cl_6) gave the D-labelled alkyne (V) whose ^{1}H n.m.r. spectrum was identical with that of (I) except for the absence of the singlet CH_2 resonance. As for the unlabelled analogue, this alkyne underwent cyclisation on treatment with CF_3CO_2D. However, the product obtained following quenching of the solution with a large excess of aq. $NaHCO_3$ was not the expected trideuterio-derivative of (III) but instead the dideuteriated alkene (IX) whose ^{1}H n.m.r. spectrum contained a characteristic one-proton singlet resonance for the unique vinyl proton. Since the reaction medium does not provide an external proton source, this vinyl proton must be supplied by the alkyne precursor (V) itself.

From consideration of the reaction mechanism [2](Scheme), it follows that the intermediate (VII), resulting from cyclisation of the first-formed vinyl cation (VI), must rearrange by 1,3-shift of the allylic proton of the η^4-cyclopentadiene ligand to give directly the cation (VIII). Furthermore, subsequent conversion of the last cation into the product (IX) must involve specific loss of the deuterium atom of the $\overset{+}{C}$HD fragment. Such specificity of D^+ transfer was further illustrated by the finding that dissolution of (IX) in CF_3CO_2D followed by quenching (aq. $NaHCO_3$) of the solution of the resulting cation (VIII) gave back the starting alkene with no H-D exchange of the vinyl proton. The ^{1}H n.m.r. spectra of the cation (VIII) and that obtained by addition of H^+ (CF_3CO_2H) to the alkene (IX) were in accord with expectation (see Experimental) and ruled out the possibility of scrambling of the D-labels.

We interpret these findings as indicated in the Scheme. Evidence has been obtained [4] to suggest that substitution of ferrocene and its derivatives by reactive electrophiles proceeds by exo-addition of the electrophile to a cyclopentadienyl ring carbon followed by endo-proton loss from the resulting 16-electron (Fe) intermediate cation. The corresponding intermediate (VII) in the conversion of (VI) into (VIII) must undergo intra-ionic 1,3-shift[¶] of the allylic proton across the endo-face of the bridging chain (antarafacial 1,3-shift is sterically impossible), a process which locates the CHD deuterium atom of (VIII) in the exo-configuration. Since the D-isotope effect normally favours H^+ over D^+ loss in E1 reactions [5], it follows that there is a marked stereoelectronic preference for exo- over endo-deprotonation (dedeuteronation) of the conformationally immobile bridging group of the cations (II) and (VIII) which outweighs the isotope effect. For the reverse reaction, exo-protonation (deuteronation) of the double bond of (III) and (IX) is correspondingly favoured. These conclusions are in harmony with earlier work [3] which established a preference for exo-proton transfer (in the absence of adverse steric effects) in interconversions of ferrocenylalkylium ions and ferrocenylalkenes.

Experimental

For general remarks, see Part 4 [6].

[¶] The mixing of ligand π-orbitals with metal orbitals may facilitate this rearrangement which, in the absence of the metal, would be disfavoured by orbital-symmetry effects.

(Phenylpropynoyl)ferrocene (IV)

A solution of $PhC{\equiv}CCO_2H$ (1.5 g; 10 mmol) in $SOCl_2$ (50 ml) was heated under reflux for 1h and the excess of solvent was then evaporated. The crude residual $PhC{\equiv}CCOCl$ and ferrocene (3.0 g; 16 mmol) were dissolved in $CHCl_3$ (100 ml), the solution was cooled to 0^o, and powdered Al_2Cl_6 (ca. 2 g) was added in portions with stirring. The resulting deep blue solution was allowed to come to room temperature, stirred for a further 1h, then poured into ice-water. The organic layer was washed (H_2O), dried ($MgSO_4$), and evaporated, and the residue was chromatographed on Al_2O_3. Petrol eluted unchanged ferrocene (1.0 g; 33% recovery) and petrol:ether (1:1) eluted the title ketone (1.4 g; 41%), a deep maroon solid m.p. 105-106^o (lit. [7] 103-106^o); ^1H n.m.r. ($CDCl_3$) τ2.2-2.7 (m; 5H; Ph), 4.97 and 5.37 (2t; 4H; C_5H_4), and 5.71 (s; 5H; C_5H_5).

3,3-Dideuterio-3-ferrocenyl-1-phenylpropyne (V)

A solution of the ketone (IV)(1.0 g; 3.2 mmol) in benzene:ether (1:3; 20 ml) was added to a stirred suspension of $LiAlD_4$ (0.38 g) and powdered Al_2Cl_6 (1.35 g) in ether (100 ml). The mixture was stirred for 0.5h and then methanol was added carefully to destroy unchanged reducing agent. The solution was washed (H_2O), dried ($MgSO_4$), and evaporated, and the residue was dissolved in petrol and chromatographed (Al_2O_3). The same solvent eluted the title compound (0.95 g; 98%), a yellow solid m.p. 71-73^o; ^1H n.m.r. ($CDCl_3$) τ2.35-2.8 (m; 5H; Ph) and 5.65-5.95 (m+s; 9H; Fc).

3,3-Dideuterio-1-phenyl[3](1,2)ferrocenophan-1-ene (IX)

A solution of the alkyne (V)(0.3 g; 1.0 mmol) in CF_3CO_2D (3 ml; Aldrich "Gold Label"; 99 atom % D) was heated under reflux for 0.5h, then cooled, and poured with vigorous stirring into a large excess of saturated aq. $NaHCO_3$ solution. The product was extracted with ether and purified by preparative t.l.c. on SiO_2 which afforded the title compound (0.26 g; 85%), an amber liquid; ^{1}H n.m.r. ($CDCl_3$) τ2.15-2.75 (m; 5H; Ph), 3.50 (s; 1H; vinyl), and 5.5-5.6, 5.9-6.0 (2m+s; 8H; cyclopentadienyl).

Treatment of this alkene with CF_3CO_2D followed by aq. $NaHCO_3$ as in the preceding experiment gave product identical (^{1}H n.m.r.) with the starting material.

^{1}H N.m.r. Spectra of Ferrocenophanyl Cations

Solutions of the alkene (IX) in CF_3CO_2D and CF_3CO_2H gave spectra of the corresponding carbocations; the phenyl and cyclopentadienyl proton resonance patterns in these spectra were identical with those in the spectrum [2] of the cation (II), viz. τ1.9-2.7 (m; 5H; Ph), 3.68 (t; 1H), 3.91 (d; 1H), and 4.57 (d; 1H)(C_5H_3), and 5.52 (s; 5H; C_5H_5). The resonances of the bridge proton(s) were as follows; (a) (III) in CF_3CO_2H, giving (II): τ6.5-6.9 and 7.35-7.6 (AA'BB' pattern; 4H); (b) (IX) in CF_3CO_2H: τ6.2-7.2 (AB quartet; J_{AB} = ca. 18 Hz; 2H); (c) (IX) in CF_3CO_2D, giving (VIII): τ6.5 (broad s; 1H).

Acknowledgement

W.C. thanks the Northern Ireland Department of Education for a postgraduate grant.

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