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Metallation of alkynes
Part 10. Acetoxymercuration of arylferrocenylethynes[☆,☆☆]

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Abstract

Arylferrocenylhethynes compounds reacted with mercuric acetate in acetic acid yielding mercurated addition compounds, the regiochemistry of which were determined by the strongly electron-donating ferrocenyl ring. Substituent effects on the reactivity are in agreement with electrophilic reactions and rate constants are best related by σ^+. © 1999 Elsevier Science S.A. All rights reserved.

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Solvomercuration–demercuration of alkenes is a well-known reaction, largely used in organic synthesis [2]. The reaction of Hg(II) species with carbon–carbon double bonds is an electrophilic addition one, that proceeds via a cationic intermediate, which was depicted either as a carbocation or as a bridged mercurinium ion, but it is better considered now as a nonsymmetrical mercurinium ion [3,4]. The interest in the mechanism of this reaction is still alive [5], leading to comparison with bromination [5–7].

The corresponding reaction of alkynes has been much less investigated, although this fact did not prevent the use in organic synthesis [2]. Regiochemistry [8,9] and stereochemistry [8,10,11] were investigated, with results depending on the alkyne. The first kinetic investigation indicated that acetoxymercuration of alkynes is an electrophilic reaction [12]. Substituent effects and stereochemistry were investigated later, using 1-arylpropynes [13] and diarylethynes [14] as the substrates.

Our lasting interest in the mechanism of acetoxymercuration [1,12–14] made us consider the possibility of extending the investigation to arylferrocenylethynes, especially considering the possibility of a metal participation in a preliminary interaction with the electrophilic species [15]. The mechanism of reaction with mercuric acetate was previously studied on ferrocenylethyne as the substrate, showing a quite complex pattern, due to the presence of C(sp)–H [16].

We report here the results of an investigation on the acetoxymercuration of arylferrocenylethynes, a family of alkynes chosen in order to assess the effect of substituents on the regiochemistry, besides that on the reactivity and the relative importance of aryl and ferrocenyl rings.

1. Results and discussion

1.1. Preparation of substrates

Arylferrocenylethynes were prepared according to the method of Stephens and Castro [17] which we used with slight modifications. Thus, copper arylacetylide was reacted with iodoferrocene in *N*,*N*-

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[☆] Dedicated to Professor Alberto Ceccon on the occasion of his 65th birthday.

[☆☆] For Part 9, see Ref. [1].

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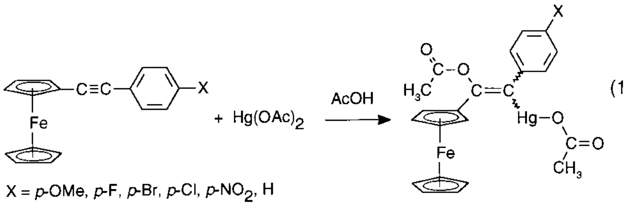


X = p-OMe, p-F, p-Br, p-Cl, p-NO_2, H

Scheme 1.

dimethylformamide. Arylferrocenylethynes pure enough for kinetic measurements (> 98% by GC) were obtained by column chromatography.

Mass spectra of arylferrocenylethynes always showed the molecular ion and a fragmentation pattern with loss of the CpFe moiety, in some cases accompanied by loss of the substituent of the aryl ring.

1.2. Product analysis

Arylferrocenylethynes were reacted with mercuric acetate in acetic acid at room temperature (Scheme 1).

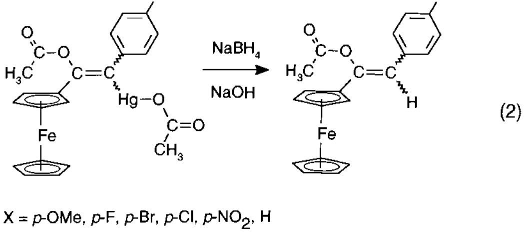
The reaction was monitored by GC analysis, following the disappearance of the alkyne, the mercurated species not being detectable.

The products from the acetoxymercuration reaction were isolated. However, they are insoluble in organic solvents and do not burn well, thus, disallowing elemental analysis. Reductive demercuration of the acetoxymercurio species, a well-established method [18] which in our hands gave the same results as X-ray analysis of crystalline mercurated compounds [19] contributed to the product analysis (Scheme 2).

During isolation of the mercurated compounds, particular care must be paid in evaporating acetic acid without heating over r.t. [14]. Molecular ions are not detectable in mass spectra, probably because the compounds are not volatile enough for EI and not soluble in matrices for FAB.

1.3. Regiochemistry

Only one of the regioisomers was detected by GC–MS analyses of the demercurated compounds (see Section 2). This is in agreement with the strong electron-releasing ability of the ferrocene moiety.



X = p-OMe, p-F, p-Br, p-Cl, p-NO_2, H

Scheme 2.

1.4. Kinetics

Kinetic experiments were performed under pseudo-first-order conditions using spectrophotometry, following the reaction up to 90–99% conversion. The acetoxymercuration of arylferrocenylethynes followed a second-order rate law, first-order in substrate and first-order in $Hg(OAc)_2$, as already found for other alkynes [1], [12–14]. The results are summarised in Table 1.

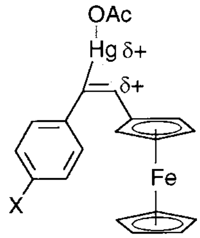
The acetoxymercuration reaction is favoured by electron-donating substituents, as expected for an electrophilic attack in the rate-determining step and in agreement with previously reported data [1,12–14].

1.5. Linear free energy relationship

In order to evaluate substituent effects quantitatively, empirical linear free energy relationships were considered. With 1-arylpropynes, the best correlation was obtained with Hammett σ values [20] for most substituents, apart from strongly electron-releasing ones [13]. On the other hand, diarylethynes and arylphenylethynes gave a very poor correlation with Hammett σ values, while two different straight lines (for electron-withdrawing and electron-donating substituents, respectively) were obtained correlating reactivities with σ^+ values [1,14].

Plotting $\log k_X$ of arylferrocenylethynes versus Hammett σ resulted again in a poor correlation, whereas a good correlation was obtained with σ^+ values (Fig. 1).

The slope is negative and relatively small ($\rho = -2.50$), thus indicating that there is not a carbocation; if we consider bromination in acetic acid of substrates that react via a carbocation intermediate (e.g. $\rho = -4.87$ with substituted styrenes [21]) and the high stability of α-ferrocenyl carbocations ([15,22]) it is evident that the amount of positive charge on the sp^2-carbon atom of the acetoxymercuration intermediate is less than unity, in agreement with the proposed structure of a nonsymmetrical mercurinium ion and in line with previous results [1,14].



Since cyclic voltammetry and molecular modelling were shown to be useful in determining substituent effects [23] an attempt was made to correlate reaction rates with redox potentials of arylferrocenylethynes [24], but no relationship was observed. A somewhat better correlation was obtained when $\log k$ values were

Table 1
Second-order rate constants for the acetoxymercuration of arylphenylethynes, $X\text{–}C_6H_4C\equiv CFc$, at 25°C

Entry	X	k_2 ($M^{-1}s^{-1}$)	$[Hg(OAc)_2]$/ [alchino]	% of reaction followed
1	H	$(8.2\pm0.4)\times10^{-2}$	20–300	90–97
2	4-OMe	$(2.05\pm0.09)\times10^{-1}$	100–1000	90–99
3	4-F	$(8.9\pm0.9)\times10^{-2}$	12–1000	82–99
4	4-Cl	$(7.1\pm0.5)\times10^{-2}$	200–7000	87–97
5	4-Br	$(7.3\pm0.8)\times10^{-2}$	9–1000	82–97
6	$4\text{-}NO_2$	$(3.5\pm0.3)\times10^{-2}$	20–100	80–95

plotted against HOMO energies, as calculated by the ZINDO/1 method (see Section 2), as shown in Fig. 2. This discrepancy might be due to solvation effects, as one referee suggested.

2. Experimental

GC analyses were carried out with a Carlo Erba HRGC 5300 Mega Series instrument, equipped with a 2 m 3% OV-17 or a 30 m × 0.25 mm capillary column.

Bruker WP80 and AM400 spectrometers were used to obtain ^1H- and ^{13}C-NMR spectra, respectively, as $CDCl_3$ solutions with TMS as the internal standard.

GC–MS analyses were performed with a Hewlett–Packard 5970B system, equipped with a Hewlett–Packard gas chromatograph.

Kinetics and spectrophotometric measurements were carried out on a Cary 1E spectrophotometer; IR spectra were recorded with a Perkin–Elmer 983 spectrophotometer.

2.1. Materials

Mercuric acetate (Merck) was a commercially available grade reagent. Ultra-pure acetic acid (Erba RSE) was used in kinetic experiments. Phenylethyne (Aldrich) was transformed into its copper(I) derivative with an aqueous solution of cuprous iodide [15].

Substituted arylferrocenylethynes were obtained by refluxing equimolar amounts of $ArC\equiv CCu$ and FcI [25] in *N*,*N*-dimethylformamide, rather than pyridine used by Castro and Stephens [17], under a nitrogen atmosphere. After the usual workup, the following arylferrocenylethynes were obtained gas chromatographically pure, after column chromatography (silica gel:hexane as the eluent). Yields were in the range 26–50%. All the compounds in their IR spectra had frequencies characteristic of monosubstituted ferrocenes (1003 and 1106 cm^{-1} [26]).

2.2. Ferrocenylphenylethyne

M.p 109–111°C. ^1H-NMR, $CDCl_3$ δ (ppm): 4.0–4.6 (complex, 9H, superimposed unsubstituted and substituted cyclopentadienyl (Cp) rings), 7.2–7.6 (complex, 5H, Ph). ^{13}C-NMR data is listed in Table 2. GC–MS (*m*/*z*): cluster around 286 (M^+, Fe isotopes; MF, 286.15), cluster around 165 ($M^+ - CpFe$). IR, CCl_4, $\nu(C\equiv C)$: 2208 cm^{-1}.

2.3. Ferrocenyl(4-methoxyphenyl)ethyne

M.p 96–98°C. ^1H-NMR, $CDCl_3$ δ (ppm): 4.0–4.6 (complex, 9H, superimposed unsubstituted and substituted Cp rings), 7.1–7.7 (complex, 4H, aromatic protons). ^{13}C-NMR data is listed in Table 2. GC–MS (*m*/*z*): cluster around 316 (M^+, Fe isotopes; MF, 316.18), cluster around 301 ($M^+ - Me$, Fe isotopes), 195 ($M^+ - CpFe$). IR, CCl_4, $\nu(C\equiv C)$: 2214 cm^{-1}.

2.4. (4-Bromophenyl)ferrocenylethyne

M.p (dec.) 122–124°C. ^1H-NMR, $CDCl_3$ δ (ppm): 3.6–4.6 (complex, 12H, superimposed –OMe, unsubstituted and substituted Cp rings), 6.7–7.6 (complex, 4H, aromatic protons). ^{13}C-NMR data is listed in Table 2.

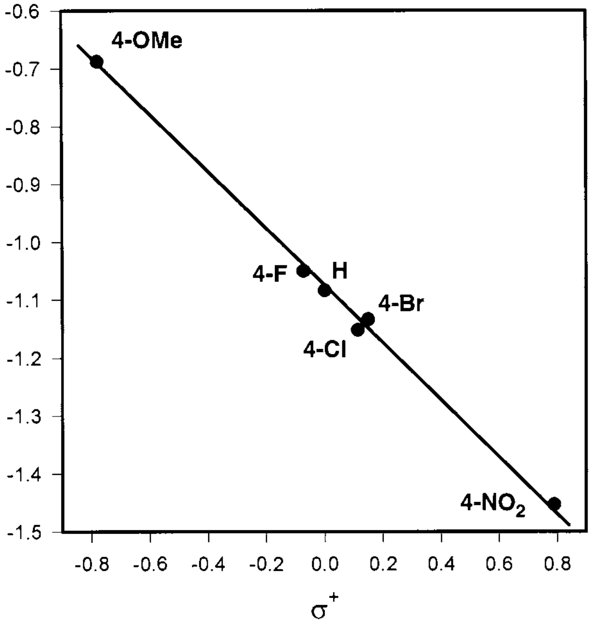


Fig. 1. Linear free energy relationship of rate constants with σ^+.

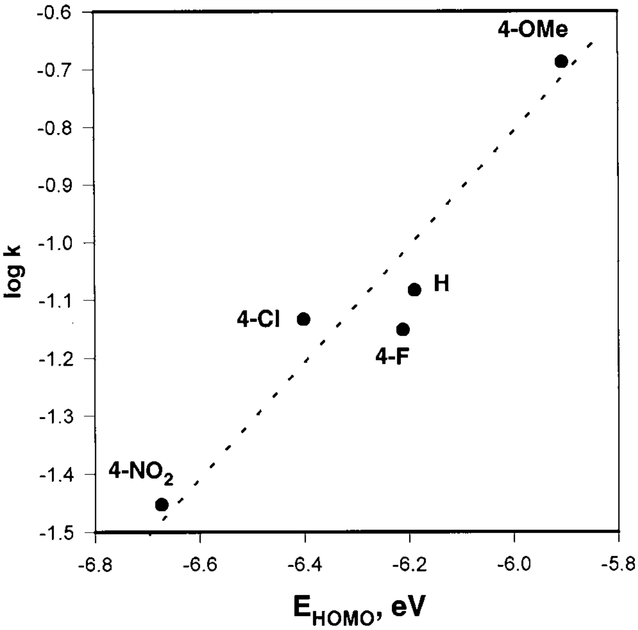


Fig. 2. Attempt to correlate rate constants with HOMO energies.

GC–MS (m/z): cluster around 364 (M^+, Fe and Br isotopes; MF, 365.05), 245.247 ($M^+ -$CpFe, Br isotopes), 163 ($M^+ -$CpFe–Br). IR, CCl_4, ν(C≡C): 2208 cm^{-1}.

2.5. (4-Chlorophenyl)ferrocenylethyne

M.p 131–133°C. ^{1}H-NMR, $CDCl_3$ δ (ppm): 4.1–4.6 (complex, 9H, superimposed unsubstituted and substituted Cp rings), 6.9–7.6 (complex, 4H, aromatic protons). ^{13}C-NMR data is listed in Table 2. GC–MS (m/z): cluster around 320 (M^+, Fe and Cl isotopes; MF, 320.60), 200.202 ($M^+ -$CpFe, Cl isotopes), 163 ($M^+ -$CpFe–Cl). IR, CCl_4, ν(C≡C): 2209 cm^{-1}.

2.6. Ferrocenyl(4-fluorophenyl)ethyne

M.p 121–122°C. ^{1}H-NMR, $CDCl_3$ δ (ppm): 4.1–4.5 (complex, 9H, superimposed unsubstituted and substituted Cp rings), 7.5–8.3 (complex, 4H, aromatic protons). ^{13}C-NMR data is listed in Table 2. GC–MS (m/z): cluster around 331 (M^+, Fe isotopes; MF, 331.15), 183 ($M^+ -$CpFe). IR, CCl_4, ν(C≡C): 2212 cm^{-1}.

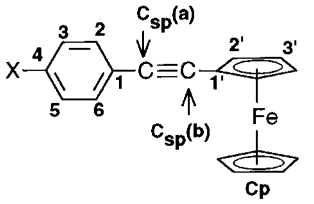
2.7. Ferrocenyl(4-nitrophenyl)ethyne

M.p 195–197°C. ^{1}H-NMR, $CDCl_3$ δ (ppm): 4.1–4.6 (complex, 9H, superimposed unsubstituted and substituted Cp rings), 6.9–7.6 (complex, 4H, aromatic protons). ^{13}C-NMR data is listed in Table 2. GC–MS (m/z): cluster around 304 (M^+, Fe isotopes; MF, 304.14), cluster around 304 ($M^+ - NO_2$, Fe isotopes), 163 ($M^+ -$CpFe–NO_2). IR, CCl_4, ν(C≡C): 2206 cm^{-1}.

2.8. Product analysis

In a typical experiment, 1 mmol of alkyne was reacted with 1.1 mmol of $Hg(OAc)_2$ in 10 ml AcOH at

Table 2
^{13}C-NMR spectra of arylferrocenylethynes in $CDCl_3$ [a]



X→	F [b]			H	OMe	Br	Cl	NO_2
C1	119.96			123.94	116.09	121.67	122.19	131.02
C2	133.24	133.16	$^3J_{CF} = 8.1$ Hz	131.36	132.85	132.77	132.58	131.75
C3	115.60	115.38	$^2J_{CF} = 22.0$ Hz	127.94	113.91	131.49	128.58	123.57
C4	163.37	160.89	$J_{CF} = 248.8$ Hz	128.23	159.17	122.94	133.63	146.35
Csp(a)	87.94			88.29	86.56	89.72	89.48	95.18
Csp(b)	84.63			85.72	85.60	84.69	84.65	84.40
C1′	65.29			65.35	66.37	64.82	65.13	53.40
C2′	68.96			68.83	68.93	68.94	69.12	69.51
C3′	71.46			71.42	71.45	71.80	71.55	71.74
Cp	70.09			69.99	70.24	69.97	70.17	70.08
X					55.29			

[a] Assigned from comparison with ^{13}C-NMR spectra of ferrocenes and calculated chemical shifts [27].

[b] J_{CF} values are in agreement with expected ones [28].

r.t., monitoring the disappearance of the substrate by GC and TLC. Acetic acid was removed under vacuum without heating above 30°C, and the residue was washed with water to remove unreacted mercuric acetate and dried.

The acetoxymercurio derivatives were insoluble in organic solvents and, when heated, decomposed without melting. Any attempt to obtain EI or FAB mass spectra failed.

Reductive demercuration was performed on a portion of the acetoxymercurio compound, suspended in water. An aqueous basic (NaOH) solution of $NaBH_4$ was added dropwise, under stirring, at 0°C. Metallic mercury separated almost immediately. The organic layer was washed with water to neutrality, dried over anhydrous Na_2SO_4, and immediately examined by GC–MS. Only one compound was always observed. All mass spectra presented a base peak with m/z corresponding to M^+ of the vinyl ester (see Scheme 2). Significant fragmentations were observed with clusters around $M^+ - Ac$ (Fe isotopes) and, more importantly, around m/z 213 (Fe isotopes). The latter is relative to $FcCO^+$ and indicates that the regioisomer is FcC(OAc)=CHAr. Finally, a peak with m/z 121 ($CpFe^+$) was always present.

2.9. Kinetic measurements

Preliminary experiments, carried out by recording spectra at subsequent times, in the range 280–320 nm, showed in most cases the presence of an isosbestic point around 290 nm, with absorbance values decreasing at wavelengths lower and increasing at wavelengths higher than this point. Kinetic experiments have been carried out under pseudo-first-order conditions. Solutions containing known concentrations of alkyne and mercuric acetate in acetic acid were separately put into the two parts of a silica cell with septum and allowed to reach 25°C in the thermostatted cell compartment of the spectrophotometer. After mixing, the absorbance variation with time was read at the appropriate wavelength. The same k_{obs} values were obtained for kinetics run at wavelengths before and after the isosbestic point. Pseudo-first-order rate constants were calculated using SigmaPlot [29].

The data are reported in Table 1, as overall second-order constants. They are mean values of several runs, carried out under conditions specified as follows (wavelengths in parentheses).

2.10. Ferrocenyl(4-methoxyphenyl)ethyne

p-$MeOC_6H_4C{\equiv}CFc$, 7.91×10^{-5} M; $Hg(OAc)_2$, 8.38×10^{-3}–8.38×10^{-2} M (275, 330 nm).

2.11. Ferrocenylphenylethyne

$FcC{\equiv}CPh$, 1.57–2.79×10^{-4} M; $Hg(OAc)_2$, 8.38×10^{-4}–8.38×10^{-2} M (275, 280, 330 nm).

2.12. Ferrocenyl(4-fluorophenyl)ethyne

p-$FC_6H_4C{\equiv}CFc$, 6.58×10^{-5}–8.22×10^{-2} M; $Hg(OAc)_2$, 8.38×10^{-4}–8.38×10^{-2} M (290, 315, 320 nm).

2.13. (4-Chlorophenyl)ferrocenylethyne

p-$ClC_6H_4C{\equiv}CFc$, 6.24–9.36×10^{-5} M; $Hg(OAc)_2$, 8.38×10^{-3}–8.38×10^{-2} M (280, 285, 320 nm).

2.14. (4-Bromophenyl)ferrocenylethyne

p-$BrC_6H_4C{\equiv}CFc$, 8.22–9.36×10^{-5} M; $Hg(OAc)_2$, 8.38×10^{-3}–8.38×10^{-2} M (270, 280, 330, 340 nm).

2.15. Ferrocenyl(4-nitrophenyl)ethyne

p-$NO_2C_6H_4C{\equiv}CFc$, 7.55×10^{-5} M; $Hg(OAc)_2$, 1.68–8.38×10^{-2} M (260, 280, 315 nm).

2.16. Determination of HOMO energy for arylferrocenylethynes

The structures of substituted arylferrocenylethynes were first optimised starting from a structure where ferrocenyl and aryl rings were coplanar. The ZINDO/1 method was used, parametrized for iron-containing compounds, as supplied by the HyperChem program [30]. The following conditions were used: total charge = 0; spin multiplicity = 1; SCF controls: convergence limit = 0.001, iteration limit = 400; accelerate convergence; overlap weighting factors: σ–$\sigma = 1$ (default), π–$\pi = 1$ (default); state: lowest; spin pairing: RHF; configuration interaction: none. Options for optimisation were as follows. Algorithm: Polak–Ribiere (conjugate gradient); termination condition: RMS gradient of 0.01 kcal Å^{-1} mol^{-1} or 2000 max. cycles; in vacuo. HOMO energies were obtained, after optimisation, by a single point calculation.

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