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One-step synthesis of aryl-capped vinylferrocenes from ferrocene and aryl-substituted oxiranes

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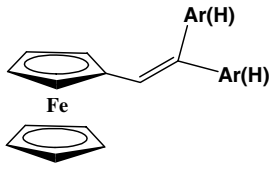
Abstract

Ferrocene reacts in methanesulfonic acid with aryl- and diaryloxiranes to afford (2-arylvinyl)- and (2,2-diarylvinyl)ferrocenes, respectively. The reaction with aryloxiranes is highly stereoselective and gives only the (*E*)-isomers. The reaction presumably proceeds via fast isomerisation of the protonated oxirane to the protonated carbonyl compound, which attacks ferrocene.

Keywords: Ferrocene; Oxirane; Friedel–Crafts reaction; Methanesulfonic acid; Alkenylation

1. Introduction

Aryl-capped vinylferrocenes **1** are important substrates for applications in materials science [1]. For example, (*Z*)- and (*E*)-1-ferrocenyl-2-(4-nitrophenyl)ethenes and related push–pull ferrocenyl compounds display large second-order optical nonlinearities useful for the development of optoelectronic and photonic devices [2–14]. On the other hand, the recently discovered organometallic antiestrogen and a potential anticancer drug, ferrocifen, contains also the backbone **1** [15,16].



1

Compounds **1** can be prepared by Wittig reaction using ferrocenyl compounds either as carbonyl components or as ylide precursors [17–21] although this way often leads to mixtures of (*E*)- and (*Z*)-isomers. Other synthetic methods for **1** involve Heck coupling reaction [22,23], olefin cross-methatesis [24], McMurry reductive coupling of ferrocenyl carbonyl compounds [15,16] and samarium diiodide-promoted condensation of these compounds with benzyl bromides [25]. All these approaches require specifically substituted ferrocenes as starting materials and, consequently, the syntheses of **1** starting from ferrocene are multi-step procedures.

In this paper, we report that **1** can be prepared directly from ferrocene and aryl-substituted oxiranes in methanesulfonic acid (MSA)–dichloromethane (DCM) mixtures as a solvent (Scheme 1). This finding, along with our earlier results [26–28], shows that there is still considerable synthetic potential in the seemingly well-elaborated electrophilic C–C forming reactions of ferrocene.

2. Results and discussion

The reactions shown in Scheme 1 were carried out by addition of oxirane dissolved in DCM to a stirred solution of ferrocene in MSA or MSA–DCM at r.t. In the

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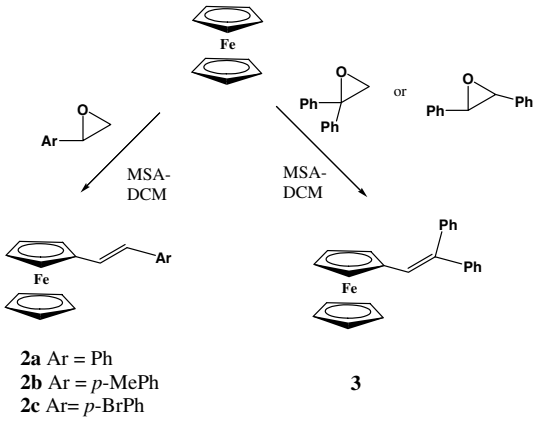


2a Ar = Ph
2b Ar = *p*-MePh
2c Ar= *p*-BrPh

3

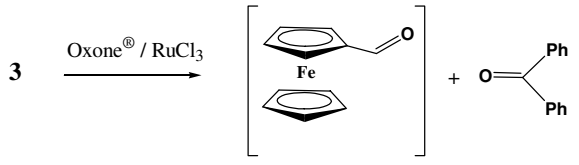
Scheme 1.

case of monoaryl-substituted oxiranes the (*E*)-styrylferrocenes **2a**–**c** were the only isolable products (Table 1). They were identified by spectral comparison with authentic samples. The (*E*)-stereochemistry was deduced from characteristic, large values of the coupling constants between the vinylic protons (c.a. 16 Hz) [19]. The (*Z*)-isomers are known to display lower values of these coupling constants (typically c.a. 12 Hz). In all reactions small amounts of ferrocene were recovered and separated from the products by flash chromatography.

Reactions of ferrocene with 2,2-diphenyloxirane and (*E*)-2,3-diphenyloxirane (*trans*-stilbene oxide) give the same product **3**. As spectral data did not allow unambiguous assignment of the substitution pattern of the ethylenic bond we oxidized this compound with Oxone® in the presence of $RuCl_3$ (Scheme 2). It is known that this reagent cleaves C=C bonds with formation of two C=O bonds [29]. We have isolated from the reaction mixture benzophenone, which confirms the presence of the C=C(Ph)$_2$ moiety in **3**. However, we were unable to isolate the second carbonyl compound formed in this reaction, ferrocene carboxaldehyde or its oxidation product, ferrocene carboxylic acid. We think that they may decompose under strongly oxidising conditions.

Table 1
Reaction of ferrocene with aryloxiranes in MSA–DCM

Oxirane	Product (% Yield)
2-phenyl-	**2a** (55)
2-(*p*-methylphenyl)-	**2b** (43)
2-(*p*-bromophenyl)-	**2c** (61)
2,2-diphenyl-	**3** (64)
(*E*)-2,3-diphenyl-	**3** (55)



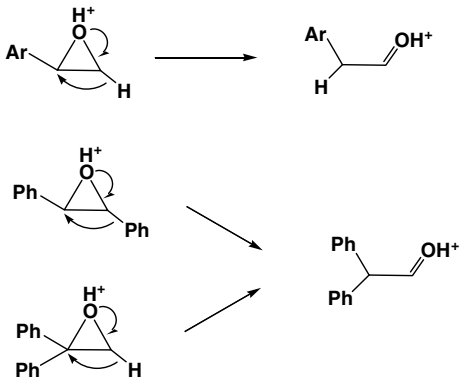
decomposed in the strongly oxidising medium

Scheme 2.

The above results suggest that reaction of ferrocene with aryloxiranes in MSA–DCM does not involve carbenium ions formed by ring-opening of oxirane. Indeed, in such a case, e.g., phenyloxirane is supposed to form Ph–CH$^+$–CH$_2$OH rather than Ph–CH(OH)CH$_2^+$, and different regiochemistry of its reaction with ferrocene would have been expected. In our opinion, the most plausible mechanism for this reaction is that involving fast rearrangement of protonated oxiranes to protonated carbonyl compounds (Scheme 3), which then attack ferrocene

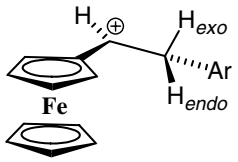
Rearrangement of oxiranes in acidic media to carbonyl compounds is a well known phenomenon [30]. Furthermore, it is well established that ferrocene reacts with protonated carbonyl compounds to give ferrocenyl alcohols or alkenes (however this reaction often lacks the selectivity) [31,32]. We have found that under the same conditions phenylacetaldehyde (product of the rearrangement of phenyloxirane) reacts with ferrocene to give **2a** in 64% yield.

Some features of the reaction described in this communication are worth noting. First, is the absence of products originating from carbenium ions formed by ring-opening of epoxides. Second, it is the selective formation of conjugated π-systems (in any case we were able to isolate products having OH groups). These two features are in sharp contrast with results obtained for reactions of epoxides with purely organic arenes [33]. E.g., methyloxirane is reported to react with benzene in the presence of a Lewis acid to give almost exclusively 2-phenyl-1-propanol (i.e., product expected for reaction of carbenium ion formed preferentially from the epoxide with the arene) [34]. Similar outcome was observed for the reaction of phenyloxirane with indole in the presence of $InBr_3$ [35]. Finally, the (*E*)-stereochemistry observed



Scheme 3.

in reaction of ferrocene with monoaryl-substituted oxiranes can be tentatively explained as a result of a stereoselective *exo*-deprotonation of the ferrocenylcarbenium ions formed from reactants in a strongly acidic medium [36], whose the most stable conformation is that minimizing steric interactions between the ferrocenyl and aryl groups (**A**).



A

In conclusion, we have found a simple, one-step synthesis of arene-capped vinylferrocenes by a Friedel–Crafts reaction of ferrocene with aryloxiranes. In our opinion, this finding can significantly extend the role of Friedel–Crafts chemistry in synthesis of specifically substituted ferrocenes required by materials science and biochemistry. We are currently studying the scope and limitations of the reported reaction.

3. Experimental

All reactions were performed under argon. Chromatographic separations were carried out on Silica gel 60 (Merck, 230–400 mesh ASTM). The NMR spectra were run on a Varian Gemini 200 BB s (200 MHz for ^{1}H), IR spectra on a FT-IR Nexus and mass spectra on a Finnigan MAT 95 spectrometer.

4. Reaction of ferrocene with aryloxiranes in MSA–DCM

Ferrocene (186 mg, 1 mmol) was dissolved in a mixture of MSA (5 ml) and dichloromethane (2 ml). To this solution aryloxirane (2 mmol), dissolved in dichloromethane (1 ml), was added dropwise and the resulting mixture was stirred at room temperature for 2 h. Quenching with ice-water (25 ml), extraction with dichloromethane and flash chromatography (eluent hexane) afforded the products. Small amounts of ferrocene were also isolated from the first yellow fraction.

The spectral data presented below are identical with those obtained for the authentic samples of **2a–c** and **3** [18,20,24,37]:

(*E*)-1-ferrocenyl-2-phenylethene (**2a**): (200 MHz, $CDCl_3$): δ 7.48–7.24 (m, 5H), 6.91 (d, $J = 16.1$ Hz, 1H), 6.72 (d, $J = 16.1$ Hz, 1H), 4.49 (t, $J = 1.6$Hz, 2H), 4.31 (t, $J = 1.6$ Hz, 2H), 4.16 (s, 5H).^{13}C NMR (50 MHz, $CDCl_3$): δ 137.82, 128.58, 126.83, 126.71, 125.95, 125.71, 83.29, 69.18, 68.99, 66.84.

(*E*)-1-ferrocenyl-2-(4-methylphenyl)ethene (**2b**): ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.33 (d, $J = 8.0$ Hz, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 6.83 (d, $J = 16.1$ Hz, 1H), 6.66 (d, $J = 16.1$ Hz, 1H), 4.45 (s, 2H), 4.26 (s, 2H), 4.13 (s, 5H), 2.34 (s, 3H).^{13}C NMR (50 MHz, $CDCl_3$): δ 136.60, 135.16, 129.36, 126.03, 125.82, 125.70, 83.64, 69.89, 68.89, 66.77, 21.22. MS (EI): *m/z* 302 (M^+), 237 ($M - Cp^+$), 179 ($M - CpFe^+$). HRMS: 302.07481.Calcd for $C_{19}H_{18}Fe$: 302.07579.

(*E*)-1-ferrocenyl-2-(4-bromophenyl)ethene (**2c**): ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.44 (d, $J = 8.6$ Hz, 2H), 7.28 (d, $J = 8.6$ Hz, 2H), 6.87 (d, $J = 16.1$ Hz, 1H), 6.62 (d, $J = 16.1$ Hz, 1H), 4.45 (t, $J = 1.7$ Hz, 2H), 4.29 (t, $J = 1.7$ Hz, 2H), 4.14 (s, 5H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 136.80, 131.66, 127.85, 127.19, 124.67, 120.24, 82.87, 69.25, 66.97. MS (EI): *m/e* 366 and 368 (M^+ for ^{79}Br and ^{81}Br, respectively). HRMS: *m/e* 365.96990. Calcd. for $C_{18}H_{15}(^{79}Br)$ Fe 365.97065.

1-ferrocenyl-2,2-diphenylethene (**3**): Yield 64% using 2,2-diphenyloxirane and 55% using (*E*)-2,3-diphenyloxirane. ^{1}H NMR (200 MHz, $CDCl_3$):δ 7.23–7.44 (m, 10H), 6.79 (s, 1H), 4.12 (s, 5H), 4.10 (t, $J = 1.8$ Hz, 2H), 3.82 (t, $J = 1.8$ Hz, 2H).^{13}C NMR (50 MHz, $CDCl_3$): δ 142.76, 141.03, 138.37, 130.14, 128.59, 128.22, 127.17, 126.72, 126.56, 125.98, 81.85, 69.49, 69.11, 68.89. MS (EI): *m/z* 364 (M^+), 299 ($M - Cp^+$). HRMS: 364.09144. Calcd. for $C_{24}H_{20}Fe$: 364.08994.

5. Oxidation of 3 with Oxone®–$RuCl_3$

To a solution of **3** (60 mg, 0.165 mmol) in acetonitrile (2.5 ml) and (water 1.5 ml) were added $NaHCO_3$ (200 mg), $RuCl_3$ (0.175 ml of a 0.035 M aqueous solution), and Oxone® (2×100 mg within 15 min). The mixture was stirred at r.t for 2 h and poured onto water. Extraction with dichloromethane and flash chromatography (silicagel, dichloromethane–hexane 7:3) afforded benzophenone (22 mg, 72%) as a colouress oil, identified by spectral comparison with an authentic sample. HR MS: *m/e* 182.07359 (calcd. for $C_{13}H_{10}O$ *m/e* 182.07317).

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