Direct Arylation of Ferrocenylacetylenes and Ferrocenylethenes under Autocatalytic Meerwein Conditions

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Ferrocenylacetylene reacts with arenediazonium in various solvents to form (arylethynyl)ferrocenes and, depending on the solvent composition, the corresponding Meerwein-type arylethenes. Applied to vinylferrocene, this autocatalytic reaction even leads to double arylation. Ferrocenyl–yne–ene systems, however, give rise to radical quenching on the olefinic moiety with partial arylation.

Introduction

Conjugated polyaromatic compounds, substituted by redox tunable metallocenes, represent promising candidates for the design of new nonlinear optical materials.[1] As a consequence, the development of efficient and straightforward synthetic approaches is stimulated. This prompted us to investigate the applicability of the widely established Meerwein reaction[2] to suitable ferrocene derivatives. Serving as reducing agents for the diazonium ions,[3] they can generate the required active aryl radicals in a self supplying manner.

Results and Discussion

Any pathway preferred by a reaction system that contains substituted ferrocenes in the presence of diazotation mixtures, either undergoing classical ring arylation[4] or following a formal Meerwein sequence, should offer a great potential for versatile derivations. Thus, standard diazotation conditions according to Gomberg, Bachmann, and Hey[4] result in spontaneous effervescence and darkening of the reaction mixture on combining ethynylferrocene in acetone with an aqueous hydrochloric solution of freshly prepared arenediazonium salts. (α-Chloro-β-arylvinyl)ferrocenes (25–30%) and acetylferrocene (20%) can be isolated as the main products, but even (arylethynyl)ferrocenes are formed directly in considerable quantities (5%). Subsequent elimination with strong bases (t-BuOK in THF) simply converts the HCl adducts (see Table I, compounds **1**, **3**, and **5**) to the corresponding (arylethynyl)ferrocenes (compounds **2** and **4**).[5]

With the exception of the Richter synthesis for cinnoline ring closures,[6] where the diazene substructure remains in the intramolecular cyclization product, the conversion of arenediazonium salts with ethyne derivatives by arylation and concomitant addition of a nucleophile has found minor utilization in preparative organic chemistry due to unacceptably poor yields.

In general, ethynylferrocene behaves quite differently from common arylacetylenes when it is subjected to electrophilic substitution conditions. With respect to phenomenological and mechanistic aspects, our findings are very similar to those reported for the reaction of ethynylferrocene with arylsulfenyl chlorides.[7] Kinetic monitoring revealed very rapid formation of terminally substituted [(arylthio)ferrocenyl]acetylenes in competition with acid addition. However, the normally expected electrophilic additions to the triple bond were not observed. This was attributed to a primary interaction between the electrophilic sulfur species and the iron center, leading to a transition state which preferably governs the ligand to form a substitution rather than an addition product. It should be noted that the related vinylferrocene exclusively gives addition products on the same treatment with ArSCl derivatives.[8] On the basis of the above considerations, a mechanism similar to the well-confirmed Gomberg–Bachmann–Hey reaction sequence for core arylations[4] should be operative for the present system as well.

Reductive precursor-catalyzed dediazoniation obviously results in the attack of the hereby generated aryl radical at the terminal alkyne carbon, leading to a stabilized α-ferrocenylvinyl cation. Subsequent neutralization by suitable nucleophiles or proton elimination finally leads to the corresponding ferrocenylvinyl and ferrocenylethynyl products, respectively. Since acidic aqueous conditions facilitate water addition on the starting ferrocenylacetylene to form acetylferrocene, the resulting product composition supports the evidence of the proposed pathways. Treatment of ethynylferrocene with arenediazonium in the presence of auxiliary bases, though, successfully prevents this side reaction, yielding only the expected β-arylation products. The highest yields were achieved in aqueous acetone (acetone/water (3:1)) in the presence of 5 equiv of CaO based on ethynylferrocene. Although arylation of vinyl derivatives in this particular combination using other electron-transfer catalysts has been reported,[9] vinylferrocene and 1-(3-methylbut-3-en-1-ynyl)ferrocene[10] did not show any Meerwein-type arylation at all when applied to this system (see Table I).

Dry DMSO proved to be an appropriate solvent as well, but increased formation of acetylferrocene occurs again in the absence of auxiliary bases. Apparently, protonation

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(4) Gmelin, L. *Gmelin, Handbuch d. Anorganischen Chemie*; Fe-Organische Verbindungen; Springer: Berlin, 1974; Vol. 14/A1, p 133.

(5) Krauch, S.; Kunz, W. *Reaktionen der Organischen Chemie*, 5th ed.; Hüthig: Heidelberg,1976; p 172.

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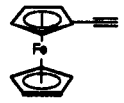
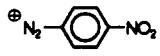
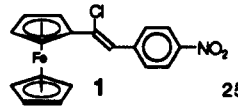
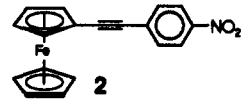
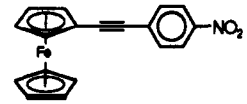
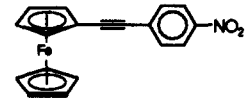
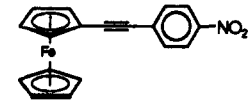
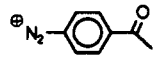
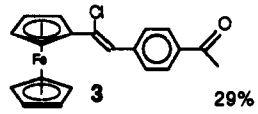
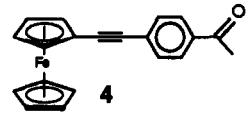
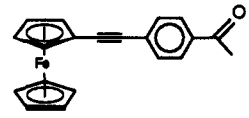
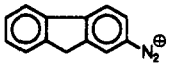
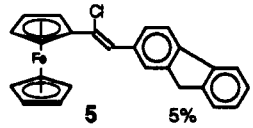
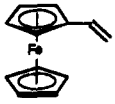
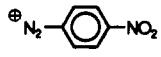
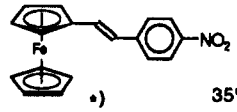
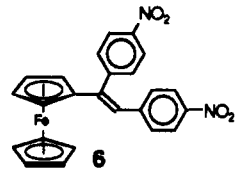
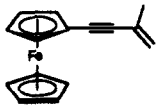
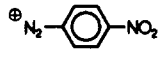
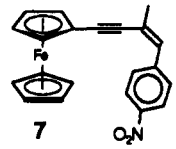
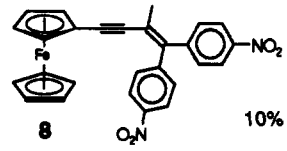
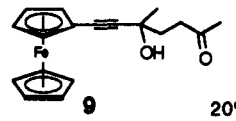
Table I. Product Compositions of Meerwein Arylations with Ferrocenyl-Substituted Ethenes and Ethynes

substrate	diazonium	system	products, compd no., % isolated		
		acetone 5 N HCl, 1 : 1	 1 25%	 2 5%	21%
		acetone / water 3 : 1, CaO		 47%	—
		DMSO		 18%	48%
		DMSO / pyridine		 8%	—
		acetone 5 N HCl, 1 : 1	 3 29%	 4 5%	20%
		acetone / water 3 : 1, CaO		 36%	—
		acetone 5 N HCl, 1 : 1	 5 5%		18%
		DMSO	 a) 35%	 6 5%	
		DMSO	 7 22%	 8 10%	
		acetone / water 3 : 1, CaO	 9 20%		

[a] Reference 16.

gives rise to the oxidation of ethynylferrocene, involving some oxysulfonium intermediate. In analogy to aqueous systems, base addition suppresses the formation of acetylferrocene as well. Pyridine, however, did not only eliminate the generation of acetylferrocene in anhydrous DMSO but concomitantly reduced the overall yields of Meerwein-type arylation products. Since pyridine and arenediazonium salts strongly tend to build some reactive arylazopyridinium complexes[11] and enhance the radical concentration of the system without further redox catalyst, other radical combinations disfavoring the desired pathway are evidently preferred.

Terminally substituted, congested ethynylferrocenes seem to be unsuitable reactants for Meerwein arylations anyway, as an attempted reaction of 4-nitrobenzenediazonium tetrafluoroborate with the dicobalt hexacarbonyl monoadduct of 1,4-diferrocenylbutadiyne[12] in anhydrous DMSO failed. Moreover, it is consistent with the expectations of the mechanistic considerations outlined above that no reaction takes place between ethynylferrocene and 4-diazobenzenesulfonate or 4-bromobenzenediazonium

(11) (a) Loewenschuss, H.; Wahl, G. H.; Zollinger, H. *Helv. Chim. Acta* **1976**, *59*, 1438. (b) Abramovitch, R. A.; Saha, G. J. *Tetrahedron* **1965**, *21*, 3297.

tetrafluoroborate. In fact, such weaker oxidants[13] are only capable of initiating the electron transfer for ferrocene ($E_{1/2}$ = 0.410 V vs saturated Ag/AgCl electrode)[14] but not for ethynylferrocene (according to our own measurements $E_{1/2}$ = 0.610 V),[12] which again confirms the necessity of a radical source process.

Experimental Section

General. Instrumentation and laboratory equipment are described elsewhere.[14] Ethynylferrocene[15] and 1-(3-methylbut-3-en-1-ynyl)ferrocene[10] were prepared according to published methods. All other starting materials were obtained from commercial suppliers and were used without further purification. The purity of all products was checked by TLC. NMR values are given in δ.

General Procedures. The preparation of 2–4 will serve to illustrate the general procedures utilized.

1-[2-(4-Nitrophenyl)ethynyl]ferrocene (2). Method A. Ethynylferrocene (0.210 g, 1.0 mmol) and CaO (0.28 g, 5.0 mmol) were dissolved/suspended in a mixture of 20 mL of acetone and 10 mL of water. The suspension was cooled to 0 °C and carefully degassed by a rapid stream of argon. A solution of 0.44 g of 4-nitrobenzenediazonium hexafluorophosphate (1.5 mmol) in another 20 mL of acetone was then added dropwise to this mixture under inert atmosphere. After 2 h of stirring at room temperature, liberation of nitrogen ceased. The dark-colored suspension was combined with 200 mL of water together with some $Na_2S_2O_4$ and extracted with ether (3 × 40 mL). The organic layer was washed with water and dried over Na_2SO_4, and the residue was finally chromatographed on basic alumina (Merck, Alox 90 (III), 70–230 mesh, flash column, 4 × 30 cm, hexane) to give 0.16 g of 1-[2-(4-nitrophenyl)ethynyl]ferrocene (2, 0.47 mmol, 47%) (see separate section for analytical data).

Method B. 4-Nitrobenzenediazonium hexafluorophosphate (0.29 g, 1.0 mmol) was added to a carefully degassed solution of 0.21 g of ethynylferrocene (1.0 mmol) in 20 mL of dry DMSO in small portions. After 2 h of stirring at room temperature and under inert atmosphere, the reaction mixture was combined with 200 mL of water together with some $Na_2S_2O_4$ and then extracted with ether (3 × 40 mL). Further workup was similar to that of method A. Yields: 0.06 g of 1-[2-(4-nitrophenyl)ethynyl]ferrocene (2, 0.18 mmol, 18%), 0.11 g of acetylferrocene (0.48 mmol, 48%).

1-[(*Z*)-1-Chloro-2-(4-acetylphenyl)ethenyl]ferrocene (3). A solution of 0.07 g of $NaNO_2$ (1.0 mmol) in 10 mL of H_2O was added dropwise to 0.14 g of 4-aminoacetophenone (1.0 mmol) in 30 mL of 5 N HCl at 0 °C. After 5 min of stirring, the aqueous solution was added rapidly to 0.21 g of ethynylferrocene in 100 mL of ice-cold acetone under inert atmosphere. Soon the reaction mixture showed spontaneous effervescence and considerable darkening while being stirred for 2 h at room temperature. When the liberation of nitrogen had ceased, the solution was combined with 200 mL of water together with some $Na_2S_2O_4$ and then extracted with ether (3 × 30 mL). The organic layer was washed with saturated $NaHCO_3$ solution and water and finally dried over Na_2SO_4. After removal of the solvent, the residue was chromatographed on basic alumina (Merck, Alox 90 (III) 70–230 mesh, flash column, 4 × 50 cm, hexane:ether = 1:1) yielding 13 mg (0.04 mmol, 4%) of 1-[2-(4-acetylphenyl)ethynyl]ferrocene (4) as the first fraction, 98 mg (0.27 mmol, 27%) of 1-[(*Z*)-1-chloro-2-(4-acetylphenyl)ethenyl]ferrocene (3) as the second fraction, and 46 mg (0.20 mmol, 20%) of acetylferrocene as third fraction (eluent: diethyl ether).

1-[2-(4-Acetylphenyl)ethenyl]ferrocene (4). 1-[(*Z*)-1-Chloro-2-(4-acetylphenyl)ethenyl]ferrocene (3, 0.37 g, 1.0 mmol) and 2.8 g of *t*-BuOK (25 mmol) in 20 mL of dry THF were refluxed for 45 min. After addition of 200 mL of water the mixture was extracted with ether (3 × 50 mL). The organic layer was washed with 2 N HCl and water and dried over Na_2SO_4. The residue was further purified by recrystallization from cyclohexane. Yield: 0.30 g (0.90 mmol, 90%).

Analytical Data. 1-[(Z)-1-Chloro-2-(4-nitrophenyl)ethenyl]ferrocene (1):[17] mp 139 °C; ^{1}H-NMR ($CDCl_3$) 4.23 (s, 5H), 4.39 (pst, 2H, *J* = 1.6 Hz), 4.66 (pst, 2H, *J* = 1.6 Hz), 6.83 (s, 1H), 8.01 (m, 4H); ^{13}C-NMR(CCl_4) 67.16, 69.77, 84.55, 118.71, 123.29, 129.14, 141.04; IR (KBr) 3108, 3090, 1618, 1591, 1522, 1513, 1340, 1264, 1116, 1109, 1002, 959, 882, 866, 823, 779, 750, 698, 547, 506, 479, 435 cm^{-1}; MS (EI, 70 eV) *m/z* 368.

1-[2-(4-Nitrophenyl)ethynyl]ferrocene (2): mp 204 °C; ^{1}H-NMR ($CDCl_3$) 4.18 (s, 5H), 4.23 (pst, 2H, *J* = 1.6 Hz), 4.45(pst, 2H, *J* = 1.6 Hz), 7.84 (m, 4H); ^{13}C-NMR(CCl_4) 67.35, 68.16, 69.88, 85.20, 120.08, 128.36, 129.08, 140.18; IR (KBr) 3056, 2203, 1973, 1894, 1680, 1591, 1510, 1485, 1439, 1346, 1312, 1286, 1184, 1121, 1070, 995, 922, 847, 831, 814, 787, 748, 721, 696, 505, 457, 443 cm^{-1}; MS (EI, 70 eV) *m/z* 331.

1-[(*Z*)-1-Chloro-2-(4-acetylphenyl)ethenyl]ferrocene (3): mp 179 °C; ^{1}H-NMR ($CDCl_3$) 2.59 (s, 3H), 4.22 (s, 5H), 4.35 (pst, 2H, *J* = 1.8 Hz), 4.64 (pst, 2H, *J* = 18 Hz), 6.82 (s, 1H), 7.85 (m, 4H); ^{13}C-NMR($CDCl_3$) 26.60, 67.35, 69.88, 85.19, 120.08, 128.36, 129.08, 140.18, 197.67; IR (KBr) 3098, 2963, 2925, 2856, 1674, 1600, 1416, 1362, 1277, 1264, 1189, 1109, 1056, 1038, 963, 954, 883, 817, 790, 696, 680, 594, 585, 547, 513, 493, 477 cm^{-1}; MS (EI, 70 eV) *m/z* 364.

1-[2-(4-Acetylphenyl)ethynyl]ferrocene (4): mp 148 °C; ^{1}H-NMR ($CDCl_3$) 2.60 (s, 3H), 4.25 (s, 5H), 4.28 (pst, 2H, *J* = 1.5 Hz), 4.53 (pst, 2H, *J* = 1.5 Hz), 7.77 (m, 4H) ; ^{13}C-NMR($CDCl_3$) 26.56, 64.31, 69.19, 70.01, 71.56, 85.21, 92.55, 128.22, 128.94, 131.31, 135.52, 197.29; IR (KBr) 3110, 3098, 3080, 2960, 2926, 2857, 2215, 1681, 1602, 1409, 1351, 1288, 1268, 1166, 1109, 1032, 1007, 962, 925, 831, 816, 692, 595, 588, 548, 519, 512, 502, 489, 472, 442 cm^{-1}; MS (EI, 70 eV) *m/z* 328.

2-[(*Z*)-2-Chloro-2-(1-ferrocenyl)ethenyl]fluorene (5): mp 115–116 °C; ^{1}H-NMR ($CDCl_3$) 3.93 (s, 2H), 4.24 (s, 5H), 4.33 (pst, 2H, *J* = 1.8 Hz), 4.65 (pst, 2H, *J* = 1.8 Hz), 6.89 (s, 1 H), 7.68 (m, 7H); ^{13}C-NMR($CDCl_3$) 36.93, 67.06, 69.39, 69.81, 86.17, 119.63, 119.97, 121.60, 125.04, 125.41, 126.81, 128.26, 130.78, 134.04, 140.83, 140.99, 141.42, 143.24, 143.64; IR (KBr) 3094, 2960, 2929, 2858, 1467, 1458, 1418, 1392, 1262, 1107, 1054, 1030, 1001, 951, 888, 822, 811, 771, 736, 533, 501, 490, 474, 423 cm^{-1}; MS (EI, 70 eV) *m/z* 410.

1-[(*E*)-2-(4-Nitrophenyl)ethenyl]ferrocene:[16] mp 197 °C, sublim. 152–153 °C; ^{1}H-NMR ($CDCl_3$) 4.14 (s, 5H), 4.36 (pst, 2H, *J* = 1.5 Hz), 4.50 (pst, 2H, *J* = 1.5 Hz), 6.69 (d, 1H, *J* = 16.2 Hz), 7.08 (d, 1H, *J* = 16.2 Hz), 7.83 (m, 4H); ^{13}C-NMR($CDCl_3$) 67.41, 69.34, 69.94, 81.65, 123.33, 124.14, 125.81, 132.85, 144.34; IR (KBr) 3110, 3084, 1632, 1595, 1512, 1344, 1302, 1282, 1192, 1114, 1048, 1032, 1005, 962, 937, 871, 830, 755, 700, 510, 884, 457, 430 cm^{-1}; MS (EI, 70 eV) *m/z* 333.

1-[1,2-Bis(4-nitrophenyl)ethenyl]ferrocene (6): mp 237 °C dec; ^{1}H-NMR ($CDCl_3$) 3.84 (s, 2H), 4.15 (s, 5H), 4.23 (s, 2H), 7.03 (s, 1H), 7.37 (m, 4H), 8.22 (m, 4H); ^{13}C-NMR ($CDCl_3$) 69.41, 70.03, 70.38, 85.40, 123.94, 124.31, 126.27, 126.86, 130.66, 130.96, 131.33, 132.58, 147.05, 147.79; IR (KBr) 3108, 3085, 1600, 1582, 1520, 1343, 1268, 1110, 1049, 919, 860, 852, 823, 759, 751, 709, 699, 510, 501, 488, 474 cm^{-1}; MS (EI, 70 eV) *m/z* 454.

1- [(*Z*)-3-Methyl-4-(4-nitrophenyl)but-3-en-1-ynyl]ferrocene (7):[17] mp 58 °C; ^{1}H-NMR ($CDCl_3$) 2.17 (d, 3H, *J* = 0.9 Hz), 4.22 (s, 5H), 4.30 (pst, 2H, *J* = 1.5 Hz), 4.48 (pst, 2H, *J* = 1.5 Hz), 6.57 (q, 1H, *J* = 0.9 Hz), 8.09 (m, 4H); ^{13}C-NMR ($CDCl_3$) 25.95, 64.36, 69.46, 70.07, 71.45, 86.19, 98.14, 123.53, 128.29, 130.86, 143.62, 146.25; IR (KBr) 2917, 2176, 1588, 1505, 1412, 1335, 1258, 1107, 1026, 933, 874, 833, 820, 748, 688, 511, 486, 472, 441 cm^{-1}; MS (EI, 70 eV) *m/z* 359.

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1-[3-Methyl-4,4-bis(4-nitrophenyl)but-3-en-1-ynyl]ferrocene (8): IR (KBr) 2964, 2923, 2858, 2207, 2182, 1596, 1518, 1342, 1265, 1110, 1095, 1026, 938, 878, 867, 804, 752, 697, 585, 510, 490, 471 cm^{-1}; MS (EI, 70 eV) *m/z* 493.

***rac*-1-(3-Hydroxy-3-methyl-6-oxohept-1-ynyl)ferrocene (9):** ^1H-NMR ($CDCl_3$) 1.54 (s, 3H), 1.97 (t, 2H, J = 7.2 Hz), 2.19 (s, 3H), 2.75 (t of diastereotopic H, J = 7.2 Hz), 2.76 (s, 1H), 2.78 (t of diastereotopic H, J = 7.2 Hz), 4.14 (pst, 2H, J = 1.8 Hz), 4.15 (s, 5H), 4.35 (pst, 2H, J = 1.8 Hz); ^{13}C-NMR ($CDCl_3$) 30.06, 30.59, 37.03, 39.54, 64.48, 67.88, 68.55, 69.80, 71.28, 82.16, 88.32; IR (KBr) 3367, 3098, 2977, 2907, 2263, 1701, 1412, 1377, 1358, 1298, 1259, 1205, 1175, 1151, 1132, 1105, 1063, 1030, 1005, 949, 930, 823, 654, 557, 524, 484 cm^{-1}; MS (EI, 70 eV) *m/z* 339.

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Supplementary Material Available: ^1H and ^{13}C 200-MHz NMR spectra of all compounds except 8 (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.