Synthesis and electronic spectra of 1-aryl-2-ferrocenylethylenes

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Fourteen 1-aryl-2-ferrocenylethylenes were synthesized from ferrocene and substituted phenylacetic acids. Those bearing electron-accepting groups were prepared by Wittig reaction from ferrocenylmethyltriphenylphosphonium iodide and aromatic aldehydes. Relationship between the electronic spectra, especially of the so-called *d*—*d* band at about 440 nm and the effect of substituent of the title products was investigated.

Исходя из ферроцена и замещенных фенилуксусных кислот, было синтезировано 14 1-арил-2-ферроценилэтиленов. 1-Арил-2-ферроценилэтилены, содержащие электронноакцепторные заместители, были получены по реакции Виттига из иодида ферроценилметилтрифенилфосфония и ароматических альдегидов. Изучается зависимость электронных спектров, особенно так называемой *d*—*d* полосы около 440 нм, полученных этиленов от влияния заместителя.

Our preceding papers concerned the electronic spectra of arylferrocenes [1] and ferrocenyl analogues of chalcones [2]; no linear relationship between λ_{max} of the *d*—*d* band and the character of the substituent of arylferrocenes has been found. A fairly good correlation of λ_{max} of the *d*—*d* band with σ^+ constants of substituents was ascertained with arylferrocenium cations [1]; a good correlation was found for both λ_{max} of *d*—*d* band and *K* band at 310 nm with σ constants of substituents with ferrocene analogues of chalcones. Investigation of electronic spectra of 1-aryl-2-(*p*-nitrophenyl)ethylenes showed a considerable dependence of the *K* band position upon character of the substituent [3, 4].

This paper is aimed to examine the dependence of electronic spectra of a series of suitably substituted 1-aryl-2-ferrocenylethylenes synthesized for this purpose, upon character of the substituent.

Experimental

Majority of the starting substituted phenylacetic acids were commercially available chemicals. *p*-Tolylacetic, *p*-ethylphenylacetic, and *m*-bromophenylacetic acids were obtained from the corresponding methyl esters; the latter were prepared by oxidation of substituted acetophenones with thallium nitrate according to [5]. Ferrocenylmethyltriphenylphosphonium iodide was synthesized according to [6].

Melting points were determined on a Kofler micro hot-stage, the ^{1}H NMR spectra of $CDCl_3$ solutions were measured with a Tesla BS 487 apparatus operating at 80 MHz; the values are relative to tetramethylsilane. The electronic spectra of 5×10^{-5} M-n-hexane solutions were recorded in digital form with a Perkin—Elmer, model 450 spectrophotometer; the exact λ_{max} value was determined by the method according to *Erikson* [7].

Arylacetylferrocenes I—XII

Anhydrous $AlCl_3$ (22 mmol) was added to a stirred solution of arylacetyl chloride (20 ml) and ferrocene (20 mmol) in dichloromethane (70 cm^3) at a reflux temperature. After a 3 h stirring the mixture was cooled, water (50 cm^3) was added and the organic material was taken into dichloromethane. The combined extracts were washed with a saturated solution of $NaHCO_3$ and with water. The extract was dried with Na_2SO_4, dichloromethane was distilled off and the residue was chromatographed over alumina, the eluent being benzene—ethyl acetate (volume ratio = 19 : 1). The first chromatographic band afforded the unreacted ferrocene, the second one the respective arylacetylferrocene, which was crystallized from acetone—n-hexane. Results are listed in Table 1. The third band usually yielded a small amount of 1,1′-bis(arylacetylferrocene).

1-Aryl-2-ferrocenylethylenes XIII—XXIV

Arylacetylferrocene (16 mmol) was added to a solution of $LiAlH_4$ (20 mmol) in tetrahydrofuran (100 cm^3). The mixture was refluxed for 4 h, cooled and 20 % hydrochloric acid (50 cm^3) was cautiously added, whilst stirring was continued at room temperature for 5 h. The organic material was extracted with dichloromethane after addition of $NaHSO_3$ and worked up as already mentioned. Chromatography over an alumina column with benzene as eluent afforded 1-aryl-2-ferrocenylethylenes; these were crystallized from acetone—n-hexane. Results are listed in Table 2. The unreacted starting product was isolated from the second chromatographic band. The electronic spectra of 1-aryl-2-ferrocenylethylenes are presented in Table 3 (compounds *XIII—XXIV*).

Preparation of 1-ferrocenyl-2-arylethylenes XXV—XXVIII by Wittig reaction

Potassium carbonate (6.5 mmol) in water (0.3 cm^3) was successively added to a stirred solution of ferrocenylmethyltriphenylphosphonium iodide (5 mmol) in dry dioxan (20 cm^3). To this mixture the respective substituted (*m*-, *p*-NO_2, *p*-CHO, *p*-CN) benzaldehyde (5 mmol) was added and the temperature was rised to boiling point. The reaction course was

Table 1

Arylacetylferrocenes $FcCOCH_2—C_6H_4X$

Compound	X	Formula	M_r	w_i(calc.)/% w_i(found)/% C	H	Fe	M.p./°C	Yield/%
I	H	$C_{18}H_{16}FeO$	304.17	71.08	5.29	18.36	128—130	78
				71.18	5.40	18.60		
II	*p*-CH_3O	$C_{19}H_{18}FeO_2$	334.20	68.23	5.43	16.70	91—92	65
				68.36	5.34	16.67		
III	*p*-C_2H_5O	$C_{20}H_{20}FeO_2$	348.23	68.99	5.79	16.04	118—119	61
				68.92	5.68	16.06		
IV	*p*-Cl	$C_{18}H_{15}ClFeO$	338.62	63.86	4.47	16.49	118—121	72
				63.89	4.47	16.45		
V	*m*-Cl	$C_{18}H_{15}ClFeO$	338.62	63.86	4.47	16.49	86—89	59
				63.90	4.48	16.70		
VI	*m*-CH_3	$C_{19}H_{18}FeO$	318.20	71.72	5.70	17.55	75—77	63
				71.79	5.75	17.55		
VII	*p*-CH_3	$C_{19}H_{18}FeO$	318.20	71.72	5.70	17.55	113—115	67
				71.60	5.75	17.61		
VIII	*p*-F	$C_{18}H_{15}FFeO$	323.16	67.11	4.68	17.33	116—118	71
				67.45	4.76	17.86		
IX	*m*-F	$C_{18}H_{15}FFeO$	323.16	67.11	4.68	17.33	95—96	74
				67.48	4.70	17.83		
X	*m*-Br	$C_{18}H_{15}BrFeO$	383.07	54.43	3.94	14.58	74—77	54
				54.78	4.00	14.63		
XI	*p*-C_2H_5	$C_{20}H_{20}FeO$	332.23	72.30	6.06	16.80	67—69	63
				73.20	6.23	16.60		
XII	*m*-CH_3O	$C_{19}H_{18}FeO$	334.20	68.23	5.43	16.70	88—89	66
				67.98	5.42	16.73		

Table 2

1-Aryl-2-ferrocenylethylenes $FcCH = CH—C_6H_4X$

Compound	X	Formula	M_r	w_i(calc.)/% w_i(found)/% C	H	Fe	M.p./°C	Yield/%
XIII	H	$C_{18}H_{16}Fe$	288.17	75.03	5.59	19.38	119—120	65.2
				74.98	5.60	19.23		
XIV	*p*-OCH_3	$C_{19}H_{18}FeO$	318.20	71.48	5.67	17.49	121—126	73.2
				71.75	5.84	18.07		
XV	*p*-OC_2H_5	$C_{20}H_{20}FeO$	322.23	72.31	6.06	16.81	129—131	59.1
				72.23	6.05	16.86		
XVI	*p*-Cl	$C_{18}H_{15}ClFe$	322.62	67.02	4.69	17.31	152—155	64.5
				69.32	5.05	17.43		
XVII	*m*-Cl	$C_{18}H_{15}ClFe$	322.62	67.02	4.68	17.31	101—103	61.6
				68.62	4.88	17.56		
XVIII	*m*-CH_3	$C_{19}H_{18}Fe$	302.20	75.53	6.00	18.48	94—96	59.1
				76.00	6.02	18.22		
XIX	*p*-CH_3	$C_{19}H_{18}Fe$	302.20	75.53	6.00	18.48	130—132	74.3
				75.74	5.97	17.24		
XX	*p*-F	$C_{18}H_{15}FFe$	306.14	70.61	4.93	18.24	156—157.5	62.5
				70.62	5.02	18.21		
XXI	*m*-F	$C_{18}H_{15}FFe$	306.14	70.61	4.93	18.24	99—100	37.8
				70.69	5.01	18.79		

Table 2 (Continued)

Compound	X	Formula	M_r	w_i(calc.)/% w_i(found)/% C	H	Fe	M.p./°C	Yield/%
XXII	*m*-Br	$C_{18}H_{15}BrFe$	367.67	58.89	4.11	15.21	—	98.6
				58.85	3.99	15.25		
XXIII	*p*-C_2H_5	$C_{20}H_{20}Fe$	316.23	75.96	6.37	17.66	80—87	91.2
				75.55	5.54	17.33		
XXIV	*m*-OCH_3	$C_{19}H_{18}FeO$	318.20	71.48	5.67	17.49	69—72	81.1
				71.58	5.81	17.29		
XXV	*m*-NO_2	$C_{18}H_{15}FeNO_2$	333.17	64.89	4.53	16.76	151.5—152.5	16.5
				64.84	4.52	16.78		
XXVI	*p*-CN	$C_{19}H_{15}FeN$	313.18	72.87	4.82	17.83	190—192	58
				72.88	4.82	17.75		
XXVII	*p*-CHO	$C_{19}H_{16}FeO$	316.19	72.15	5.10	17.66	169.5—170	20
				73.00	5.56	17.42		
XXVIII	*p*-NO_2	$C_{18}H_{15}FeNO_2$	333.17	64.89	4.53	16.76	198	58
				64.73	4.62	16.68		
XXIX	*p*-NH_2	$C_{18}H_{17}FeN$	303.19	71.30	5.68	18.42	183—185.5	75
				71.44	5.70	18.38		
XXX	*m*-NH_2	$C_{18}H_{17}FeN$	303.19	71.30	5.68	18.42	144.5—147	86
				71.28	5.63	18.45		

Table 3

Ultraviolet spectra of 1-ferrocenyl-2-arylethylenes

Compound	$\lambda_{max\,I}$/nm	$\frac{\varepsilon}{dm^3\,mol^{-1}\,cm^{-1}}$	$\lambda_{max\,II}$/nm	$\frac{\varepsilon}{dm^3\,mol^{-1}\,cm^{-1}}$	$\lambda_{max\,III}$/nm	$\frac{\varepsilon}{dm^3\,mol^{-1}\,cm^{-1}}$	σ
I	303.0	18260.0	262.0	13000.0	452.5	875	0.00
II	304	25579.6	267.8	15442.0	452	968.8	–0.27
III	306.5	28007.0	269	16503.5	451.5	1031.5	–0.28
IV	307	26488.2	267.5	15889.8	453	1311.8	0.23
V	301.5	22306.4	265	16515.2	454	1424.2	0.37
VI	305	23036.6	264.5	14403.8	453	1992.1	–0.07
VII	305.5	23770.0	263	15303.4	452.5	945.7	–0.17
VIII	299	18950.7	259.3	14253.9	452	946.8	0.06
IX	306.5	19585.1	262	13633.4	455.5	1131.6	0.34
X	303	24704.2	262.6	16324.6	454	1031.6	0.39
XI	302.5	18449.4	261	13222.1	452.5	1124.7	–0.15
XII	307.5	21710.7	259.5	14323.7	451.5	1001.6	0.05
XIII	308	28587.3	258	25477.6	459	1954.7	0.71
XIV	322.5	53352.9	274.5	25648.6	466	2720.1	0.66
XV	332.5	21308.3	285	—	465.5	2443.6	0.42
XVI	349	25422.2	—		483	4491.1	0.78
XVII	312	22930.1	—	—	448	706	–0.66
XVIII	306	19660.2	276	13353.1	453	918.1	–0.16

monitored by thin-layer chromatography. The mixture was filtered after about 4 h, when the reaction was through, and the solvent was removed under reduced pressure. The residue was chromatographed on an alumina-packed column (Brockmann II-neutral) the eluents being light petroleum, which separated triphenylphosphine oxide (its traces were removed from the product by fractional crystallization), and benzene. The first chromatographic band yielded traces of *cis* derivatives, the second one the corresponding *trans* derivatives; these were crystallized from benzene—n-hexane. Results are listed in Table 2 (compounds *XXV*, *XXVI*).

1-Ferrocenyl-2-(4-aminophenyl)ethylene (XXIX)

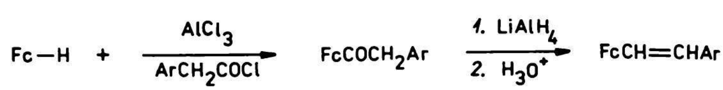
Zinc (1.03 g; 15 mmol) was added to 1-ferrocenyl-2-(4-nitrophenyl)ethylene (0.7 g; 2.1 mmol) in acetone (10 cm^3); the mixture was refluxed for 15 min, then NH_4Cl (0.5 g) in water (2 cm^3) and additional zinc (1 g) were added. The content was heated for 40 min, the insoluble substances were filtered off and washed with acetone. The acetone layers were combined, the solvent was removed and the residue was chromatographed on a silica gel column, benzene—ethyl acetate (volume ratio = 19:1) being the eluent. The first band afforded the unreacted starting material, the next one was rechromatographed to furnish *XXIX*, m.p. 183—185.5 °C (acetone), in a 75 % yield (0.48 g).

1-Ferrocenyl-2-(3-aminophenyl)ethylene (XXX)

According to the above-mentioned procedure 0.55 g (yield = 86 %) of the title product, m.p. 144.5—147 °C, was obtained from 0.7 g (2.1 mmol) of 1-ferrocenyl-2-(3-nitrophenyl)ethylene.

Results and discussion

In principle, the 1-aryl-2-ferrocenylethylenes could be prepared by Wittig reaction and its Horner modification from ferrocenylmethyltriphenylphosphonium iodide [6] or dimethyl ferrocenylmethylphosphonate [8] and substituted benzaldehydes, or alternatively by elimination of water from alcohols obtained by reduction of arylacetylferrocenes [9]. The method described by *Sutherland* [8], shown in Scheme 1 was found advantageous for its simplicity



Scheme 1

The advantage of this method is, *inter alia,* the formation of pure *trans* isomers. The Friedel—Crafts acylation of ferrocene with arylacetyl chlorides proceeded without complications and the arylacetylferrocenes were obtained in 54—78 % yields without paying attention to optimization. This method failed when attempting to synthesize *p*-nitrophenylacetylferrocene. Ferrocene was only oxidized to ferrocinium salt. The required acid chlorides were prepared by reacting the respective acid with thionyl chloride in excess; for *m*-methoxy derivative the acid chloride had to be prepared with phosphorus trichloride. The structure of the product was backed even with ^{1}H NMR spectra, which are quite similar and therefore, we present here only that for phenylacetylferrocene: $\delta = 3.9$ ppm (s, 2H, CH_2), $\delta = 4.10$ ppm (s, 5H, C_5H_5), $\delta = 4.40$ ppm (t, 2H, H_α), $\delta = 4.80$ ppm (t, 2H, H_β), $\delta = 7.07$ ppm (m, 5H, C_6H_5).

Reduction of arylacetylferrocenes and the following elimination of water proceeded smoothly to afford 1-aryl-2-ferrocenylethylenes; the required ethylenes were isolated in a 38—75 % yield per arylacetylferrocene entering the reaction. Even here, yields of this reaction were not tried to be optimized. The ^{1}H NMR spectra of 1-aryl-2-ferrocenylethylenes are very similar excepting the region of benzene protons; 1-phenyl-2-ferrocenylethylene exemplifies the characteristic data: $\delta = 3.99$ ppm (s, 5H, C_5H_5), $\delta = 4.13$ ppm (t, 2H, H_α), $\delta = 4.45$ ppm (t, 2H, H_β), $\delta = 6.80$ ppm (d, 1H, Fe—CH), $\delta = 6.76$ ppm (d, 1H, $J_{AB} = 16.3$ Hz, Ph—CH), $\delta = 7.30$ ppm (m, 5H, C_6H_5). All ethylenes prepared were shown to be *trans* isomers. The ^{1}H and ^{13}C NMR spectra of all synthesized ferrocenyl analogues of stilbene will be published elsewhere [10].

1-Aryl-2-ferrocenylethylenes having electron-accepting groups (*m*-, *p*-NO_2, *p*-CHO, *p*-CN) attached to aryl were prepared from ferrocenylmethyltriphenylphosphonium iodide and then appropriately substituted benzaldehydes by Wittig reaction in wet dioxan according to [11] (Scheme 2). The reaction proceeded well giving only traces of *cis* isomers

$$FcCH_2\overset{(+)}{P}(C_6H_5)_3\overset{(-)}{I} + Ar{-}CHO \xrightarrow[K_2CO_3]{dioxan} Fc{-}CH{=}CH{-}Ar$$

Scheme 2

Removal of triphenylphosphine oxide was succeeded by crystallization.

Attempt to synthesize the dimethylamino derivative of stilbene by treatment of ferrocenylmethyltriphenylphosphonium iodide with *p*-dimethylaminobenzaldehyde failed. Therefore, amino derivatives of stilbene were prepared by reduction of the corresponding nitro derivatives. An attempt to reduce selectively the nitro group of 1-ferrocenyl-2-(4-nitrophenyl)ethylene with tin dichloride by a method described by *Bellamy* [12] for preparation of anilines resulted in a total decomposition of the ferrocenyl derivative. For this reason the compounds were reduced with zinc in the presence of NH_4Cl [13]; the required products were obtained in high yields in this way.

The electronic spectra of 1-aryl-2-ferrocenylethylenes are characteristic of three significant absorption bands. The band at $\lambda = 450$ nm can be ascribed in line with [14] to a *d—d* transition of iron electrons, that at $\lambda \sim 305$ nm is the so-called *K*

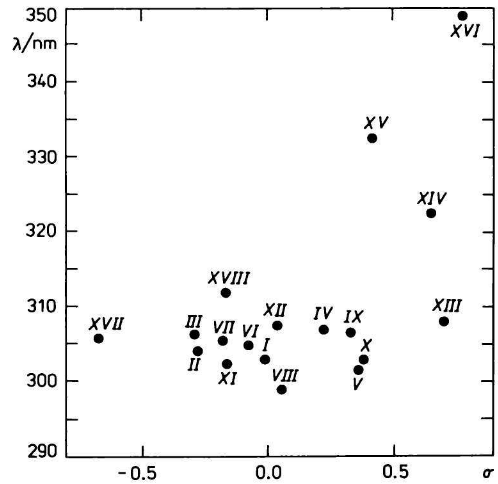


Fig. 1. Dependence between the position of the *K* band ($\lambda = 300$ nm) of 1-aryl-2-ferrocenylethylenes and character of the substituent.

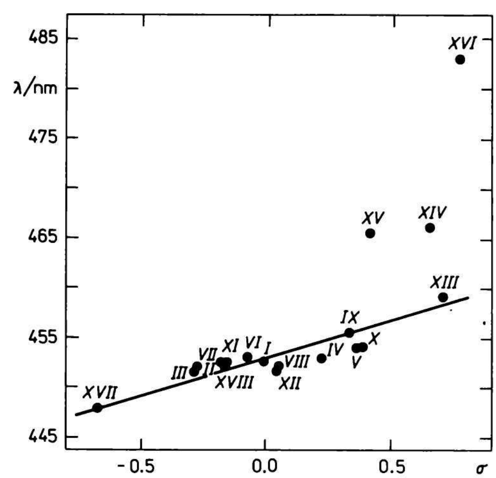


Fig. 2. Dependence between the position of the *d—d* band ($\lambda = 450$ nm) of 1-aryl-2-ferrocenylethylenes and character of the substituent.

band associated with the $\pi \rightarrow \pi^*$ transition of electrons of ligand, and that at $\lambda = 265$ nm belongs to the so-called local $\pi \rightarrow \pi^*$ transition of the substituted benzene (*cf.* [3]). Position of all three bands is only feebly dependent on the substituent nature (*cf.* Table 3); Fig. 1 shows this phenomenon for *K* band, Fig. 2 for *d—d* band. The *d—d* band at $\lambda = 450$ nm reveals the distribution of correlations into two parts. For this band (excepting *p*-CHO, *p*-CN, and *p*-NO_2 derivatives) $\varrho = 6.32$, $r = 0.889$, $s_\varrho = \pm 1.00$.

Comparison of correlation between λ_{max} of the *d—d* band of 1-aryl-2-ferrocenylethylenes and a substituent with analogous correlations for arylferrocenes and ferrocene analogues of chalcones [1, 2] makes it evident that 1-aryl-2-ferrocenylethylenes are more close to arylferrocenes; these also reveal a more significant dependence of the *d—d* band position on the substituent with strongly electron-accepting substituents only.

As it follows from relationships of the position of *d—d* band reported as yet to the character of substituent, a prominent dependence of position of this band could be only anticipated when the covalent character between iron and cyclopentadiene rings becomes pregnant, this being just supported by electron-accepting substituents on the cyclopentadienyl ring [15].

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