

Friedel—Crafts Acetylation of Ferrocene Analogues of Benzophenone, Diphenylmethane and Stilbene

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Friedel—Crafts acetylation of ferrocenyl aryl ketones, ferrocenylaryl-methanes and 1-ferrocenyl-2-arylethenes was carried out, aryl being phenyl, 2-thienyl, 2-furyl and ferrocenyl, respectively. The reactivity of the mentioned aromates is discussed. The preparation of 1-ferrocenyl-2-arylethene is studied.

It has been found [1–5] ferrocene to be substantially more reactive towards electrophilic reagents than benzene. The same conclusion was reported by *Schlögl* [6] who acetylated benzylferrocene according to Friedel—Crafts. A preferential acetylation on 2-thienyl moiety occurred when ferrocenyl(2-thienyl)methane was subjected to such an intracompetitive reaction and from this finding he deduced that the reactivity of thiophene is greater than that of ferrocene. We reported [7] acetylation of 1-ferrocenyl-3-aryl-2-propene-1-ones and 3-ferrocenyl-1-aryl-2-propene-1-ones according to Friedel—Crafts. Based upon our results we assumed that in those systems ferrocene is essentially more reactive than benzene, even more reactive than thiophene and approximately as reactive as furan. The same results were obtained also when studying competitive acetylations of ferrocene—thiophene and ferrocene—furan mixtures [7].

This paper deals with Friedel—Crafts acetylation of ferrocenyl aryl ketones, ferrocenylarylmethanes and 1-ferrocenyl-2-arylethenes, aryl being phenyl, 2-thienyl, 2-furyl and ferrocenyl.

In connection with the acetylation of 1-ferrocenyl-2-arylethenes, we studied the method of their preparation either by various modifications of Wittig reaction, or by Horner modification of Wittig reaction.

Experimental

Melting points were determined on a Kofler micro hot-stage. Chromatography was carried out over Brockmann alumina (Reanal, Budapest, activity II).

Benzoylferrocene, 2-thienoylferrocene, 2-furoylferrocene and ferrocenoylferrocene were prepared according to *Schlögl* [6]. The reaction time was prolonged up to 14 hours only when preparing ferrocenoylferrocene; thus, the yield raised to 83% in contrast to 12% reported in [8]. M.p. of benzoylferrocene, 2-thienoylferrocene, 2-furoylferrocene and ferrocenoylferrocene is in accord with [9, 6, 10] and [8], respectively. Ferrocenylaryl-methanes were prepared from the proper ketones by reduction with $\text{LiAlH}_4/\text{AlCl}_3$ complex according to [6]. M.p. of benzylferrocene, ferrocenyl(2-thienyl)methane and diferrocenyl-methane is in agreement with [9, 6] and [8], respectively. M.p. of ferrocenyl(2-furyl)methane was found to be 31°C (light petroleum).

Preparation of 1-ferrocenyl-2-phenylethene

Ferrocenylmethyltrimethylammonium iodide (5.58 g, 0.014 mole) and triethyl phosphite (11 g, 0.071 mole) in 25 ml of dry dimethylformamide were placed into a 50 ml three-necked flask provided with a mechanical stirrer, reflux condenser, calcium chloride tube and a dropping funnel. Under stirring, this mixture was heated at 160–170°C for one hour. After cooling, *t*-potassium butoxide (7.96 g, 0.071 mole) prepared from *t*-butanol (23.15 ml) and potassium (2.8 g, 0.071 g-atom) in dry benzene (25 ml) was added. The reaction mixture was heated once more while stirring up to 160°C and the heating was immediately removed. The flask was cooled under running water and benzaldehyde (1.5 g, 0.014 mole) in dry dimethylformaldehyde was added to the stirred mixture which was heated anew to 130°C and allowed to cool by standing. The reaction product was poured into ice-cold water, extracted with benzene and dried with Na₂SO₄.

The solvent was removed by distillation and the residue was purified through a 50 × 3 cm column of alumina, benzene—petroleum 2 : 1 being the solvent system. Yield 2.26 g (55.1%); m.p. 118–120°C is in accord with [11].

When the reaction mixture consisting of ferrocenyltrimethylammonium iodide and triethyl phosphite was heated for one hour and then poured into water and extracted with diethyl ether a product oily in nature was obtained after evaporation of the solvent. The substance was chromatographed over alumina with benzene; a viscous liquid — ethyl ferrocenylmethylphosphonate — was the main product.

For C₁₅H₂₁FeO₃P (336.15) calculated: 16.61% Fe, 9.21% P; found: 16.16% Fe; 9.22% P.

IR bands at 1000 cm⁻¹ (m) and 1103 cm⁻¹ (m) indicative of the unsubstituted cyclopentadiene ring in ferrocene, 1248 cm⁻¹ (νP=O) and 1160 cm⁻¹ (m) (νP—O in P—O—C₂H₅).

According to the same method 1-ferrocenyl-2-(2-thienyl)ethene, 1,2-diferrocenylethene and 1-ferrocenyl-2-(2-furyl)ethene were prepared. Their respective m.p. 151–152°C and 267–269°C are consistent with those given in [12 and 11], whereas that of 1-ferrocenyl-2-(2-furyl)ethene was found to be 112–113°C (ethanol).

Some modifications of Wittig synthesis for preparation of 1-ferrocenyl-2-arylethenes were attempted, both the solvent and the catalyst being varied. Results are listed in Table I.

Acetylation of benzoylferrocene (I)

To benzoylferrocene (*I*) (1.45 g, 0.005 mole), in dry methylene chloride (25 ml) in a 100 ml flask provided with a mechanical stirrer, reflux condenser, calcium chloride tube and a dropping funnel, acetyl chloride (1.2 g, 0.0075 mole) and anhydrous aluminium chloride (2 g, 0.015 mole) in methylene chloride (25 ml) were added during 1/2 hour. The intensive stirring was continued at room temperature for additional 4 hours. The reaction mixture was then poured into cold water and the water layer was extracted with methylene chloride. The combined extracts were washed with water, dried and the solvent was distilled off. The residue was chromatographed over a 35 × 2.5 cm column of alumina benzene with 3% of ethyl acetate being the solvent system. A smaller amount of the starting material was isolated from the first band and 1-acetyl-1'-benzoylferrocene (*Ia*) (0.95 g, 57% yield) from the latter one. M.p. of *Ia* 72–73°C (acetone—light petroleum) corresponds with [13].

Table 1

A preparation survey of 1-ferrocenyl-2-arylethenes

No.	Reaction components	Catalyst	Solvent	Product	Yield %	Modification according to
1	$\text{FcCH}_2\text{P}^+(\text{C}_6\text{H}_5)_3\text{I}^-$	benzaldehyde	phenyllithium	diethyl ether	<i>IX</i>	43 [11]*
2	$\text{FcCH}_2\text{P}^+(\text{C}_6\text{H}_5)_3\text{I}^-$	benzaldehyde	<i>t</i> -sodium amylate	benzene	<i>IX</i>	52 [42]
3	$\text{FcCH}_2\text{P}^+(\text{C}_6\text{H}_5)_3\text{I}^-$	benzaldehyde	phenyllithium	diethyl ether + + 1,2-dimethoxyethane	<i>IX</i>	40.6 [41]
4	$\text{FcCH}_2\text{P}^+(\text{C}_6\text{H}_5)_3\text{I}^-$	furfural	phenyllithium	diethyl ether	<i>XI</i>	48 [11]
5	$\text{FcCH}_2\text{P}^+(\text{C}_6\text{H}_5)_3\text{I}^-$	2-thiophenecarb- aldehyde	phenyllithium	diethyl ether	<i>X</i>	54.4 [11]
6	$\text{C}_6\text{H}_5\text{CH}_2\text{P}^+(\text{C}_6\text{H}_5)_3\text{Cl}^-$	ferrocenecarbaldehyde	phenyllithium	diethyl ether	<i>IX</i>	38 [11]
7	$\text{FcCH}_2\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$	benzaldehyde	<i>t</i> -potassium butoxide	dimethylformamide	<i>IX</i>	55 —
8	$\text{FcCH}_2\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$	furfural	<i>t</i> -potassium butoxide	dimethylformamide	<i>XI</i>	56 —
9	$\text{FcCH}_2\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$	2-thiophenecarb- aldehyde	<i>t</i> -potassium butoxide	dimethylformamide	<i>X</i>	55 —
10	$\text{FcCH}_2\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$	ferrocenecarbaldehyde	<i>t</i> -potassium butoxide	dimethylformamide	<i>XII</i>	15.2 —
11	$\text{C}_6\text{H}_5\text{CH}_2\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$	ferrocenecarbaldehyde	<i>t</i> -potassium butoxide	dimethylformamide	<i>IX</i>	56 [43]

Fc = ferrocenyl $\text{C}_{10}\text{H}_8\text{Fe}$.

* 1-Ferrocenyl-2-arylethenes were so far prepared by this method only.

*Acetylation of (2-thienoyl)ferrocene (II), (2-furoyl)ferrocene (III)
and ferrocenoylferrocene (IV)*

The procedure is the same as given with *I*. 1-Acetyl-1'-(2-thienoyl)ferrocene (*IIa*), m.p. 80–81°C (acetone—light petroleum) was isolated in 62% yield (1.05 g) when started with 0.005 mole (1.5 g) of *II*.

1-Acetyl-1'-(2-furoyl)ferrocene (*IIIa*), m.p. 89°C (acetone—light petroleum), yield 65% (1.05 g) from 0.005 mole (1.4 g) of *III*.

1-Acetyl-1'-(ferrocenoyl)ferrocene (*IVa*), m.p. 179–181°C (acetone), yield 54.5% (0.6 g) and 1-acetyl-1'-(1'-acetylferrocenoyl)ferrocene (*IVb*), m.p. 198–201°C (acetone), yield 4.5% (0.05 g) from *IV* (1 g, 0.0025 mole), AlCl_3 (1 g, 0.0075 mole) and acetyl chloride (0.25 g, 0.003 mole).

Acetylation of benzylferrocene (V)

Benzylferrocene (2 g, 0.007 mole), acetic anhydride (16 g, 0.15 mole) and phosphoric acid (2 ml 85%, 0.03 mole) were heated at 90°C for 10 minutes in a 100 ml three-necked flask provided with a stirrer and a reflux condenser with calcium chloride tube. The reaction mixture was poured into ice-cold water, extracted with benzene and the combined benzene extracts were thoroughly washed with water. Benzene after drying with Na_2SO_4 was distilled off and the residue was chromatographed over a 35 × 2.5 cm alumina column benzene being the eluent. The first band afforded a negligible amount of starting material, the second band gave 1-benzyl-2-acetylferrocene *Va* in 6.8% yield (0.15 g). M.p. 76°C (acetone—light petroleum). 1-Benzyl-1'-acetylferrocene *Vb* was isolated from the third band in 43% yield (0.95 g); m.p. 79–81°C (acetone—light petroleum) agrees with that reported in [6].

Acetylation of ferrocenyl(2-furyl)methane (VI)

Ferrocenyl(2-furyl)methane (1.8 g, 0.0066 mole) and acetic anhydride (4.1 g, 0.04 mole) in dry benzene (25 ml) was placed into a 100 ml three-necked flask provided with a stirrer and a reflux condenser with calcium chloride tube. To this mixture 85% phosphoric acid (1.5 ml, 0.022 mole) was added and stirring was continued at room temperature for additional two hours. The content of the flask was then moderately heated at reflux temperature for 1/2 more hour, poured into ice-cold water and extracted with benzene. The combined benzene layers were water washed, dried with sodium sulfate and benzene was removed. The residue was chromatographed over alumina with benzene. The first band afforded the starting material *VI* (0.5 g, 28%), the second one ferrocenyl(5-acetyl-2-furyl)methane *VIa* (0.80 g, 40%); m.p. 99–100°C (acetone—light petroleum). 1'-Acetylferrocenyl(5-acetyl-2-furyl)methane *VIb* (0.1 g, 4%) was eluted with benzene—3% ethyl acetate; m.p. 58–59°C (acetone—light petroleum).

Acetylation of ferrocenyl(2-thienyl)methane (VII)

The reaction was carried out as described above with substance *VI*. Starting from 1.85 g (0.0066 mole), ferrocenyl(2-thienyl)methane (*VII*), (1 g, 54%) of (*VII*) was recovered from the first band, 0.35 g (14%) ferrocenyl(5-acetyl-2-thienyl)methane (*VIIa*) from the second and 0.23 g (10%) (1'-acetylferrocenyl)(5-acetyl-2-thienyl)methane (*VIIb*) from the third one. M.p. of *VIIa* and *VIIb*, 147–148°C and 114–116°C (acetone—light petroleum), respectively, are consistent with those given in [6].

Acetylation of diferrocenylmethane (VIII)

The reaction was carried out as described with substance VI. Starting from diferrocenylmethane (VIII) (2.55 g, 0.0066 mole), 2 g (80%) VIII was recovered from the first band, 0.2 g (7%) ferrocenyl(2-acetylferrocenyl)methane (VIIIa) from the second, 0.08 g (3%) bis(2-acetylferrocenyl)methane (VIIIb) from the third and 0.18 g (6.4%) bis(1'-acetylferrocenyl)methane (VIIIc) from the fourth band. Their melting points were found to be 105–108°C (substance VIIIa), 240°C with decomposition (substance VIIIb) and 113–116°C (substance VIIIc) when crystallized from acetone–light petroleum.

Acetylation of 1-ferrocenyl-2-phenylethene (IX)

1-Ferrocenyl-2-phenylethene (1.5 g, 0.005 mole) and acetyl chloride (0.39 g, 0.005 mole) in methylene chloride (25 ml) were placed into a 100 ml three-necked flask provided with a stirrer, reflux condenser with a calcium chloride tube and a dropping funnel. While cooling with ice-cold water and stirring, anhydrous aluminium chloride (0.66 g, 0.005 mole) in methylene chloride (25 ml) was added. Stirring was continued at room temperature for three hours, the reaction mixture was poured into ice-cold water and extracted with methylene chloride. The combined extracts were thoroughly washed with water, dried with sodium sulfate, the solvent was removed and the distillation residue was chromatographed on an alumina 40 × 1.5 cm column, benzene–petroleum being the eluent, 0.95 g (63%) of the starting material was separated from the first band and 0.15 g (9%) 1-(2-acetylferrocenyl)-2-phenylethene (IXa) from the second one. M.p. 139–140°C (acetone–light petroleum). Upon acetylation condition described for substance V, the yield of product IXa raised to 26%, nevertheless no starting material was recovered.

*Acetylation of 1-ferrocenyl-2-(2-thienyl)ethene (X)**Method A*

The reaction was carried out as described for substance IX. Starting from 1-ferrocenyl-2-(2-thienyl)ethene (1.5 g, 0.005 mole), 0.6 g (40%) (X) was recovered from the first band, 0.2 g (12.2%) 1-ferrocenyl-2-(5-acetyl-2-thienyl)ethene (Xa) was isolated from the second and 0.08 g (3.7%) 1-(1'-acetylferrocenyl)-2-(5-acetyl-2-thienyl)ethene (Xb) from the third one. M.p. of Xa 191–193°C (petroleum), m.p. of Xb 139–141°C (acetone–petroleum).

Method B

1-Ferrocenyl-2-(2-thienyl)ethene (X) (1.5 g, 0.005 mole) and acetic anhydride (2 g, 0.02 mole) in dry benzene (50 ml) were placed into a 100 ml three-necked flask provided with a stirrer and a reflux condenser with calcium chloride tube. 85% phosphoric acid (0.4 ml, 0.005 mole) was added to the reaction constituents and the solution was kept stirred at reflux temperature for two hours. It was then poured into water, extracted with benzene and worked up as described under acetylation of IX. Yield: 0.75 g (50%) of recovered X, 0.27 g (16%) of 1-ferrocenyl-2-(5-acetyl-2-thienyl)ethene Xa; m.p. 191–193°C is in accord with that given in method A.

Table 2

Analytic data of the synthesized substances

Substance	Molecular formula	<i>M</i>	Calculated (found)				Yield ^a %	M.p. °C (Kofler)
			% C	% H	% Fe	% S		
<i>Ia</i> *	C ₁₉ H ₁₆ FeO ₂	332.18	68.69	4.85	16.81		57	72—73
			68.83	4.59	16.74			
<i>IIa</i>	C ₁₇ H ₁₄ FeO ₂ S	338.21	68.37	4.17	16.51	9.48	62	80—81
			60.20	4.28	16.41	9.30		
<i>IIIa</i>	C ₁₇ H ₁₄ FeO ₃	322.14	63.38	4.38	17.33		65	89
			63.12	4.47	17.20			
<i>IVa</i>	C ₂₃ H ₂₀ Fe ₂ O ₂	440.11	62.76	4.58	25.37		54.5	179—181
			62.59	4.42	25.34			
<i>IVb</i>	C ₂₅ H ₂₂ Fe ₂ O ₃	482.14	62.27	4.59	23.16		4.5	198—201
			62.59	4.73	22.81			
<i>Va</i>	C ₁₅ H ₁₈ FeO	318.20	71.71	5.70	17.55		6.8	76
			71.39	5.34	17.35			
<i>Vb</i> **	C ₁₅ H ₁₈ FeO	318.20	71.71	5.70	17.55		43	79—81
			72.01	5.65	17.63			
<i>VI</i>	C ₁₅ H ₁₄ FeO	266.12	67.69	5.30	20.98		67	31
			67.43	5.22	21.03			
<i>VIa</i>	C ₁₇ H ₁₆ FeO ₂	308.16	66.26	5.23	18.12		40	99—100
			66.12	5.04	17.90			
<i>VIb</i>	C ₁₉ H ₁₈ FeO ₃	353.20	65.12	5.18	15.94		4	58—59
			65.33	5.14	15.56			
<i>VIIa</i> **	C ₁₇ H ₁₆ FeOS	324.23	62.97	4.97	17.22	9.88	14	147—148
			62.77	4.83	17.16	9.62		
<i>VIIb</i> **	C ₁₉ H ₁₈ FeO ₂ S	366.26	62.30	4.95	15.24	8.75	10	114—116
			62.44	4.82	15.38	8.60		
<i>VIIIa</i>	C ₂₃ H ₂₂ Fe ₂ O	426.12	64.82	5.20	26.21		7	105—108
			65.12	4.90	25.83			
<i>VIIIb</i>	C ₂₅ H ₂₄ Fe ₂ O ₂	468.16	64.13	5.16	23.85		3	240
			63.96	5.02	23.91			
<i>VIIIc</i>	C ₂₅ H ₂₄ Fe ₂ O ₂	468.16	64.13	5.16	23.85		6.4	113—116
			64.29	5.39	23.47			
<i>IXa</i>	C ₂₀ H ₁₈ FeO	330.21	72.74	5.49	16.91		9	139—140
			72.53	5.59	16.90			
<i>Xa</i>	C ₁₈ H ₁₆ FeOS	336.24	64.29	4.79	16.60	9.53	16	191—193
			64.13	4.32	16.27	9.40		
<i>Xb</i>	C ₂₀ H ₁₈ FeO ₂ S	378.27	63.50	4.79	14.76	8.47	3.7 ^b	139—142
			63.67	4.59	14.67	8.32		
<i>XI</i>	C ₁₆ H ₁₄ FeO	278.13	69.09	5.07	20.07		56	112—113
			68.93	5.13	19.84			
<i>XIa</i>	C ₁₈ H ₁₆ FeO ₂	320.17	67.52	5.03	17.44		14	129—131
			67.34	5.27	17.47			
<i>XIIa</i>	C ₂₄ H ₂₂ Fe ₂ O	438.23	65.77	5.06	25.57		4.5	185—187
			65.94	4.72	25.14			

Substances designated by an asterisk * and ** were prepared by other methods than given in [13] and [6].

a) The yield is calculated on starting material; substantial amounts of the starting material were recovered.

b) It is formed reacting the starting material with CH₃COCl/AlCl₃.

*Acetylation of 1-ferrocenyl-2-(2-furyl)ethene (XI)**Method A*

The reaction was carried out as described for substance *IX*. 1-Ferrocenyl-2-(2-furyl)ethene (1.4 g, 0.005 mole), acetyl chloride (0.39 g, 0.005 mole) and anhydrous stannic chloride (0.8 g, 0.005 mole) afforded starting material (*XI*) 0.75 g (49%) and 1-ferrocenyl-2-(5-acetyl-2-furyl)ethene (*XIa*) 0.01 g (0.6%), m.p. 129–131°C (petroleum).

Method B

Proceeded as described for substance *X*, method *B*. 1.4 g (0.005 mole) of *XI* yielded starting material (*XI*, 0.75 g, 55%), 1-ferrocenyl-2-(5-acetyl-2-furyl)ethene (*XIa*, 0.22 g, 14%), identical with that obtained by method *A*.

Acetylation of 1,2-diferrocenylethene (XII)

Proceeded as given for substance *X*, method *B*. 1,2-Diferrocenylethene (*XII*, 0.8 g, 0.002 mole), acetic anhydride (0.8 g, 0.008 mole) and 85% phosphoric acid (0.15 ml, 0.002 mole) furnished starting material (*XII*, 0.34 g, 42%) and 1-ferrocenyl-2-(1'-acetylferrocenyl)ethene (*XIIa*, 0.04 g, 4.5%), m.p. 185–187°C (ethanol) (Table 2).

Spectral measurements

Ultraviolet spectra of substances under study were measured in 4×10^{-5} mole ethanolic solutions (spectral grade, Spolana, Neratovice) with a Perkin–Elmer-450 spectrophotometer. Cell width 1 cm, resolution 1, time constant 1, speed 5 (1 : 1). The measured values are listed in Table 3.

Infrared spectra of the described substances were taken with a Zeiss UR-20 spectrophotometer in the 700–2000 cm^{-1} range using an NaCl prism. The wavenumber scale was calibrated by means of a polystyrene foil. Samples were measured in nujol suspension the nujol spectrum being compensated. Absorption width 0.02 mm. The obtained values are given in the text.

Results and Discussion

Friedel–Crafts acetylation was carried out under such conditions so that the substitution should proceed to the first stage only.

Upon acetylation the substitution of ferrocenyl aryl ketones takes place always at the unsubstituted cyclopentadiene ring of ferrocene (into position 1') no matter whether phenyl, 2-thienyl or 2-furyl stood for aryl. On the other hand, a small amount of diacetyl derivative *IVb* was obtained when acetylating diferrocenyl ketone (Chart 1).

The acetylation was in all cases good, the yield being about 60%.

Some ferrocenylarylmethanes were already acetylated. Benzylferrocene and ferrocenyl(2-thienyl)methane was acetylated by *Schlögl* and *Pelousek* [6]. They found that the substituent entered the unsubstituted cyclopentadiene ring of ferrocene upon acetylation of benzylferrocene. On acetylation of ferrocenyl(2-thienyl)me-

Table 3

UV spectra and R_F values of the described substances

No.	λ_{\max} (nm)	$\log \epsilon$	λ_{\max} (nm)	$\log \epsilon$	λ_{\max} (nm)	$\log \epsilon$	R_F^a
I	245	4.35	278 sh	4.13	355	3.34	0.63
Ia	220	4.50	266	4.35	345 sh	3.50	0.25
II	252	4.25	294	4.27	372	3.37	0.66
IIa	220 sh	4.49	292	4.35			0.27
III	236 sh	4.22	293	4.37	370	3.37	0.57
IIIa	220	4.52	294	4.41	370	3.50	0.18
IV	237	4.46	275	4.31	360	3.68	0.58
IVa			270	4.44	355	3.73	0.21
IVb	220	4.69	268	4.55	355	3.80	0.03
V			264	3.62	322*	3.12	0.73
Va	224 sh	4.53	264	4.04	335	3.20	0.60
Vb	226	4.53	264	4.09	337	3.41	0.52
VI			254 sh	3.71	320*	3.28	0.69
VIa			283	4.48			0.56
VIb	226	4.49	280	4.54	335	3.44	0.12
VII	230 sh	4.15			325*	3.10	0.76
VIIa			263	4.21	293	4.31	0.64
VIIb	256 sh	4.47	267	4.38	289	4.40	0.26
VIII			258 sh	3.94	322*	3.41	0.75
VIIIa	227 sh	4.40	266 sh	3.98	377 sh	3.24	0.60
VIIIb	223	4.62	266	4.28	325	3.59	0.52
VIIIc	226	4.73	268	4.31	330	3.64	0.15
IX	208	4.75	263	4.39	305	4.57	0.76
IXa	205	4.84	258	4.21	310	4.44	0.64
X	208	4.59	260 sh	4.09	320	4.52	0.74
Xa	242	4.30	270 sh	4.05	365	4.52	0.60
Xb			264 sh	4.28	365	4.60	0.20
XI	208	4.61	268	4.27	312	4.60	0.75
XIa					355	4.08	0.57
XII			240 sh	4.60	315	4.50	0.80
XIIa			242	4.65	310	4.53	0.56

a) R_F determined on Silufol 254 (Kavalier, Votice), SiO₂ layer, developing system benzene—ethyl acetate (8 : 2).

* Measured in solutions $c = 4 \times 10^{-3}$ mole⁻¹.

sh = shoulder.

thane, they ascertained that the substituent preferentially enters the thiophene ring. We acetylated ferrocenylarylmethanes, where phenyl, 2-thienyl, 2-furyl and ferrocenyl stood for aryl, with acetic anhydride in benzene, or, in the case of benzylferrocene, without any solvent phosphoric acid being the catalyst. Yields of those acetylations were found to be up to 40%. Noticeable amounts of starting material were recovered. When attempting acetylation according to Schlögl with aluminium chloride or stannic chloride as catalysts, we obtained considerably impure products and, in those cases where 2-thienyl or 2-furyl stood for aryl, a decomposition of starting material took place resulting in a substantial loss of the reaction product.

Our results confirm Schlögl's conclusions. A mixture of monoacetyl derivative (VIIa) and diacetyl derivative (VIIb) was obtained in the ratio 1.4 : 1 when ace-

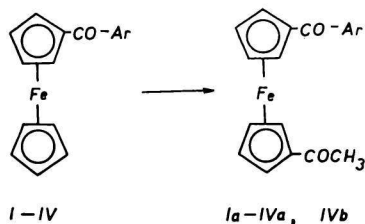


Chart 1

I Ar = phenyl; *II* Ar = 2-furyl; *III* Ar = 2-thienyl; *IV* Ar = ferrocenyl; *Ia* Ar = phenyl; *IIa* Ar = 2-furyl; *IIIa* Ar = 2-thienyl; *IVa* Ar = ferrocenyl; *IVb* Ar = 1'-acetylferrocenyl.

tylating ferrocenyl(2-thienyl)methane (*VII*). Upon acetylation of ferrocenyl(2-furyl)methane (*VI*) a mixture of monoacetyl (*VIa*) and diacetyl derivative (*VIb*) was obtained in the ratio 10 : 1. Benzylferrocene (*V*) when acetylated furnished, besides 1-benzyl-1'-acetylferrocene (*Vb*) isolated by Schlögl, 1-benzyl-2-acetylferrocene (*Va*) in the ratio 6 : 1.

Diferrocenylmethane (*VIII*) afforded after acetylation 3 substances: (2-acetylferrocenyl)ferrocenylmethane (*VIIIa*), bis(2-acetylferrocenyl)methane (*VIIIb*) and bis(1'-acetylferrocenyl)methane (*VIIIc*) in an approximate ratio 1 : 0.4 : 1 (Chart 2)

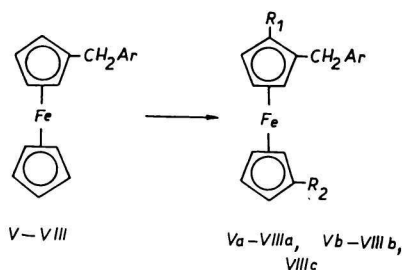


Chart 2

V Ar = phenyl; *VI* Ar = 2-thienyl; *VII* Ar = 2-furyl; *VIII* Ar = ferrocenyl; *Va* $R_1 = \text{COCH}_3$, $R_2 = \text{H}$, Ar = phenyl; *Vb* $R_1 = \text{H}$, $R_2 = \text{COCH}_3$, Ar = phenyl; *VIa* $R_1 = R_2 = \text{H}$, Ar = 5-acetyl-2-thienyl; *VIb* $R_1 = \text{H}$, $R_2 = \text{COCH}_3$, Ar = 5-acetyl-2-thienyl; *VIIa* $R_1 = R_2 = \text{H}$, Ar = 5-acetyl-2-furyl; *VIIb* $R_1 = \text{H}$, $R_2 = \text{COCH}_3$, Ar = 5-acetyl-2-furyl; *VIIIa* $R_1 = \text{COCH}_3$, $R_2 = \text{H}$, Ar = ferrocenyl; *VIIIb* $R_1 = \text{COCH}_3$, $R_2 = \text{H}$, Ar = 2-acetylferrocenyl; *VIIIc* $R_1 = \text{H}$, $R_2 = \text{COCH}_3$; Ar = 1'-acetylferrocenyl.

The acetylation of 1-ferrocenyl-2-arylethenes, where phenyl, 2-thienyl, 2-furyl and ferrocenyl stood for aryl was proceeded either by acetyl chloride, aluminium chloride being the catalyst and, in the case where 2-furyl stood for aryl, with stannic chloride as catalyst, or by acetic anhydride in benzene under catalysis of phosphoric

acid. Both methods gave low yields (10—20%); on the other hand, when the reaction was catalyzed by phosphoric acid a considerable amount of unreacted starting material (60—70%) was recovered in a relatively pure form. In those reactions where aluminium chloride or stannic chloride were the catalysts, the recovered starting material (according to R_F values) was contaminated in such an extent that it was quite impossible to get it in a crystalline form. The phenyl derivative was found to be the exception.

The acetylation of 1-ferrocenyl-2-(2-thienyl)ethene (*X*) and 1-ferrocenyl-2-(2-furyl)ethene (*XI*) attacks the position 5 of the heterocycle (Chart 3). The acetylation of 1-ferrocenyl-2-(2-thienyl)ethene, aluminium chloride being the catalyst, afforded a small amount of 1-(1'-acetylferrocenyl)-2-(5-acetyl-2-thienyl)ethene (*Xb*). Acetylation of 1-ferrocenyl-2-phenylethene (*IX*) led to 1-(2-acetylferrocenyl)-2-phenylethene (*IXa*) and acetylation of 1,2-diferrocenylethene (*XII*) to 1-ferrocenyl-2-(1'-acetylferrocenyl)ethene (*XIIb*).

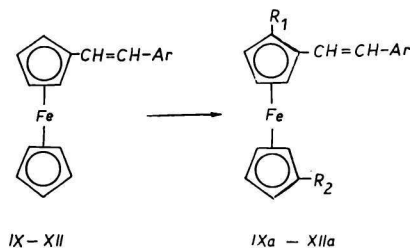


Chart 3

IX Ar = phenyl; *X* Ar = 2-thienyl; *XI* Ar = 2-furyl; *XII* Ar = ferrocenyl; *IXa* $R_1 = \text{COCH}_3$, $R_2 = \text{H}$, Ar = phenyl; *Xa* $R_1 = R_2 = \text{H}$, Ar = 5-acetyl-2-thienyl; *Xb* $R_1 = \text{H}$, $R_2 = \text{COCH}_3$, Ar = 5-acetyl-2-thienyl; *XIIa* $R_1 = R_2 = \text{H}$, Ar = 5-acetyl-2-furyl; *XIIb* $R_1 = \text{H}$, $R_2 = \text{COCH}_3$, Ar = ferrocenyl.

The obtained results show that in all those cases, where phenyl stands for aryl, the acetyl group becomes attached to ferrocene; it follows that ferrocene is always more reactive than benzene. In these cases, where 2-thienyl or 2-furyl stands for aryl, acetylation takes place either at ferrocene (as with ferrocenyl aryl ketones) or at the heterocycle (as with ferrocenylarylmethanes or 1-ferrocenyl-2-arylethenes). Based upon this finding it could be deduced that ferrocene is more reactive than thiophene and furan in the first case, whereas the reverse is true about the latter two types.

Results of the competition acetylations between ferrocene and thiophene on one hand and ferrocene and furan [7] on the other evidence that the reactivity of ferrocene is greater than that of thiophene and approximately the same as that of furan. The same order of reactivity is indirectly assumed from papers by *Pauson* [1] who found ferrocene to be more reactive than anisole and approximately as reactive as phenol, *Rosenblum* [3] (ferrocene is 3.3×10^3 more reactive than mesitylene) and *Nesmejanov* [2] (ferrocene is 5.3×10^3 more reactive than toluene) when compared with papers by *Reichstein* [14] and *Katritzky* [15] who claimed that thiophene is approximately as reactive as mesitylene and furan as reactive as phenol.

The order of reactivity of ferrocene, furan and thiophene differs according to systems in which the reactivity was examined and it can be explained as follows: The reaction course and the substitution site — whether on ferrocene or on heterocycle — will depend on the ability of the substituents (in our cases $-\text{CO}-$, $-\text{CH}_2-$ and $-\text{CH}=\text{CH}-$, or $-\text{COAr}$, $-\text{CH}_2\text{Ar}$, $-\text{CH}=\text{CHAR}$) to be involved in the stabilization of the transient σ complex. In ferrocenyl aryl ketones, the substituent is the carbonyl group which cannot only stabilize the σ complex, but also has a deactivation effect both on the heterocycle and on ferrocene. As known, there are two cyclopentadiene rings in ferrocene, and the substituent effect disappears at least partly from one ring to the other (when compared with *p*-substituted benzenes), so that the electrophilic substitution can occur relatively smoothly on the unsubstituted ring of ferrocene [16–18]. The deactivation effect of carbonyl group results in no acetylation on the furan or thiophene ring although that might be expected considering results of competition reactions [7].

In ferrocenylarylmethanes and 1-ferrocenyl-2-arylethenes, the substituents are either $-\text{CH}_2-$ or $-\text{CH}=\text{CH}-$ group which can stabilize the transient σ complex either by the +I effect and hyperconjugation ($-\text{CH}_2-$), or by its +M effect ($-\text{CH}=\text{CH}-$). Both groups should stabilize the transient σ complex equally both on ferrocene and on the heterocycle. It is, however, known that the +M effect of substituents is markedly weaker in ferrocene than in benzene [17–21]. Similarly, it is known that the methyl group increases the rate of H–D exchange in ferrocene 10 times only, whereas that in benzene 100 times [22]. From the mentioned facts it is evident that both these groups can better stabilize the σ complex which is being formed when the substituent is entering the heterocycle.

This explains even the fact why acetylation of 1-ferrocenyl-3-aryl-2-propene-1-one [7] proceeds predominantly at the heterocycle. In this case, a double bond β -carbon is attached to the heterocycle, *i.e.* a group exhibiting not only $-I$, but also a +M effect; upon acetylation of 3-ferrocenyl-1-aryl-2-propene-1-ones [7] the substitution also goes almost exclusively into ferrocene due to the carbonyl group bound to the heterocycle.

The question which is left is why the +M effect of substituents in ferrocene is less pronounced. This can be associated with the fact that:

1. The rate determining step of electrophilic substitution on ferrocene is the formation of a bond between iron and the electrophile [3, 21, 23]. It has been proved that there is no conjugation between iron and rings [3, 20, 24–26], so that the +M effect evidently cannot be involved.

2. The electrophilic substitution at ferrocene proceeds like that at benzene and consequently, the rate determining step is the formation of a σ complex [27–29]; as a result, the +M effect of substituents is not involved probably because of the 0.34 electron localized at each cyclopentadiene ring of ferrocene [30], so that ferrocene displays certain electron saturation [20].

In connection with the acetylation of 1-ferrocenyl-2-arylethenes we even verified some methods of their preparation. They can be divided into two types. Triphenylarylmethylphosphonium halide was the starting material in the first group, where both solvent and catalyst were altered. Arylmethylphosphonates belong to the second type. Results are listed in Table 1.

Best results were obtained when the precipitated trimethylethylammonium iodide was not separated when preparing diethyl ferrocenylmethylphosphonate (Table 1, experiment no. 7). If a smaller amount of the catalyst (1–4 multi-

ple), *t*-sodium butoxide, was used, this reaction did not occur. This method has an advantage since the starting material, ferrocenylmethyltrimethylammonium iodide and triethyl phosphite are easily available. All substituted ethylenes display in the infrared spectra bands at 1640 cm^{-1} and about 960 cm^{-1} characteristic of *trans* derivatives. A proof that the reaction proceeds through diethyl ferrocenylphosphonate is seen both in analyses and in infrared spectra.

To elucidate the structure of products formed during the reaction, infrared and ultraviolet spectroscopy was employed in combination with thin layer chromatography. Disappearance of bands at $1003\text{--}1010\text{ cm}^{-1}$ and $1105\text{--}1110\text{ cm}^{-1}$ [31, 32] and appearance of bands at $1115\text{--}1120\text{ cm}^{-1}$ [42] was regarded as an evidence for the 1,1'-disubstitution pattern of ferrocene. This band was diagnostic for structure determination of the acetylation product of molecules containing two ferrocenyl groups. To decide whether 1,2- or 1,3-disubstitution occurs in homoannular disubstitution at ferrocene, infrared spectroscopy cannot be taken into consideration, since the so called second *Rosenblum* rule does not hold in general [32–34]. In this case ultraviolet spectroscopy and thin layer chromatography were the tools by means of which the structure could be ascribed. As no shifts of maxima towards longer wavelengths in the acetylated products were observed upon acetylation of ferrocenyl aryl ketones and ferrocenylarylmethanes, no formation of 1,3-disubstituted products can be admitted [35, 36]. A bathochromic effect of acetylation products of 1-ferrocenyl-2-arylethenes is observed in those particular cases when the substituent enters the position 5 at the heterocycle (see Table 3). The 1,2-disubstitution is supported even by the R_F values of the homoannular disubstituted derivatives, as these reveal always higher values than the heteroannular do [36–38].

2,5-Disubstitution of furan and thiophene was evidenced, apart from ultraviolet spectra, by disappearance of the band at $750\text{--}733\text{ cm}^{-1}$ in the infrared spectrum of furan [39] and that at $730\text{--}700\text{ cm}^{-1}$ in the spectrum of thiophene [40].

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