ACETYLATION AND FORMYLATION OF SUBSTITUTED PHENYLFERROCENES

Š. Toma[a], A. Maholanyiová[a] and E. Solčaniová[b]

[a] *Department of Organic Chemistry, and*
[b] *Chemical Institute,*
Comenius University, 81 650 Bratislava

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Acetylation and formylation of phenylferrocene and 22 of its derivatives are described. The proportions of the arising isomers were determined by analysis of ^{1}H-NMR spectra of the mixtures produced by the two reactions. The 1,1′ and 1,3 isomers were found to be the main products.

Acetylation of arylferrocenes has been the subject of a few papers[1–3] and only one[4] briefly describes the formylation of phenylferrocene. The present paper deals with the effects of substituents attached to the benzene ring of phenylferrocenes on the course of their acetylation and formylation.

EXPERIMENTAL

The melting points of the acyl derivatives prepared were determined on the Kofler block. Silpearl L 100/250 (Lachema, Brno) was used for column chromatography. ^{1}H-NMR spectra of the compounds dissolved in $CDCl_3$ (99·5% ^{2}H), with tetramethylsilane as internal standard (3% v./v.), were measured in a spectrometer Tesla BS 487 at a frequency of 80 MHz. The chemical shifts were read with an accuracy of $\pm$0·005 ppm. The syntheses of the substituted phenylferrocenes are described in a previous paper[5]. Acetylation and formylation of all the phenylferrocenes were each carried out under identical conditions, so that only common procedures are described.

Acetylation

A mixture of an arylferrocene (0·007 mol), acetic anhydride (0·15 mol) and 85% phosphoric acid (0·03 mol) was heated under stirring to 90–95°C for 10 min, then poured onto crushed ice in water. The aqueous phase was extracted with several portions of benzene. The combined extracts were washed with water and dried with Na_2SO_4. The solvent was distilled off and the residue was chromatographed on a column of silica gel with benzene as eluent. In some cases combination of chromatography and crystallization gave pure 1,2- and 1,1′-isomers. A survey of the acetyl derivatives is given in Table I, their chemical shifts are listed in Table II.

Formylation

To a stirred solution of $POCl_3$ (0·013 mol) and N-methylformanilide (0·021 mol) was added an arylferrocene (0·008 mol) in small portions. The mixture was stirred 1 h at room temperature,

TABLE I

Analytical Data of Acetylated Arylferrocenes

Compound	Formula (m.v.)	Calculated % Fe	M.p., °C yield, %	Derivatives, % 1,1-	1,2	1,3
1 H[a]	$C_{18}H_{16}FeO$ (304·2)	18·36 18·45	75—83 19	67	9	24
2 4-CH_3	$C_{19}H_{18}FeO$ (318·2)	17·55 17·56	70—78 32	50	34	16
3 3-CH_2[b]	$C_{19}H_{18}FeO$ (318·2)	17·55 17·63	52—59 61	65	11	24
4 4-Cl[c]	$C_{18}H_{15}ClFeO$ (338·6)	16·49 16·35	85—90 31	49	32	19
5 3-Cl	$C_{18}H_{15}ClFeO$ (338·6)	16·49 16·33	oil 55	71	10	19
6 4-Br[d]	$C_{18}H_{15}BrFeO$ (383·1)	14·58 14·70	87—93 44	72	12	16
7 3-Br	$C_{18}H_{15}BrFeO$ (383·1)	14·58 14·04	oil 49	73	6	21
8 4-OCH_3	$C_{19}H_{18}FeO_2$ (334·2)	16·71 16·42	88—93 23	69	7	24
9[e] 3-OCH_3	$C_{19}H_{18}FeO_2$ (334·2)	16·71 17·16	131—134 20	—	—	—
10 3-CF_3	$C_{19}H_{15}F_3FeO$ (372·2)	15·01 14·59	oil 47	78	—	22
11 3,4-$(CH_3)_2$	$C_{20}H_{20}FeO$ (333·2)	16·76 15·92	oil 42	52	17	31
12 3,5-$(CH_3)_2$	$C_{20}H_{20}FeO$ (333·2)	16·76 15·89	oil 42	52	20	28
13 3,4-Cl_2	$C_{18}H_{14}Cl_2FeO$ (373·9)	14·90 14·40	oil 45	75	—	25
14 3-CF_3, 4-Cl	$C_{19}H_{14}ClF_3FeO$ (406·2)	13·75 13·54	oil 60	75	—	25
15 4-$COOC_2H_5$	$C_{21}H_{20}FeO_3$ (376·2)	14·46 13·61	oil 46	73	—	27
16 4-$OCOCH_3$	$C_{20}H_{18}FeO_3$ (362·2)	15·41 15·86	oil 43	53	20	27

[a] M.p. of the pure 1,2-isomer is 72—74°C, m.p. of the pure 1,1′-isomer is 113—114°C. [b] M.p. of the pure 1,2-isomer is 80—82°C, m.p. of the pure 1,1′-isomer is 63°C. [c] M.p. of the pure 1,1′-isomer is 101°C. [d] M.p. of the pure 1,2-isomer is 97—98°C, m.p. of the pure 1,1′-isomer is 97 to 98°C. [e] Compound 9 was acetylated in the benzene ring.

TABLE II

^{1}H-NMR Chemical Shifts of Acetylated Phenylferrocenes

Compound	$-COCH_3$		Aryl	Ferrocenyl				
				$H_{2'2}$	$H_{3'3}$	$H_{4'4}$	$H_{5'5}$	C_5H_5
1	1,1′	2·09 s	7·6—7·0 m	4·62 m	4·32 m	4·32 m	4·62 m	—
H	1,2	2·29 m		—	4·82 m	4·57 m	4·62 m	4·19 s
	1,3	2·41 s		5·23 t	—	4·90 m	4·90 m	4·05 s
2	1,1′	2·13 s	7·5—7·0 m	4·65 m	4·35 m	4·35 m	4·65 m	—
4-CH_3[a]	1,2	2·32 s		—	4·81 m	4·53 m	4·60 m	4·23 s
	1,3	2·43 s		5·22 m	—	4·92 m	4·92 m	4·08 s
3[b]	1,1′	2·13 s	7·6—9·6 m	4·65 m	4·49 m	4·49 m	4·65 m	—
3-CH_3	1,2	2·31 s		—	4·84 m	4·53 m	4·61 m	4·25 s
	1,3	2·43 s		5·23 m	—	4·91 m	4·91 m	4·08 s
4	1,1′	2·13 s	7·6—7·2 m	4·61 m	4·34 m	4·34 m	4·61 m	—
4-Cl	1,2	2·35 s		—	4·83 m	4·55 m	3·63 m	4·22 s
	1,3	2·42 s		5·20 m	—	4·90 m	4·90 m	4·05s
5	1,1′	2·21 s	7·7—7·0 m	4·75 t	4·32 t,	4·32 t	4·66 t	
3-Cl	1,2′	2·21 s		4·66 t;	4·40 t	4·40 t	4·75 t	
	1,3	2·40 s		—	4·91 m	—	—	4·25 s
				5·30 m	—	5·01 m	5·01 m	4·13 s
6	1,1′	2·13 s	7·6—7·2 m	4·62 m	4·35 m	4·35 m	4·62 m	—
4-Br	1,2	2·37 s		—	4·83 m	4·58 m	4·63 m	4·21 s
	1,3	2·42 s		5·21 m	—	4·91 m	4·91 m	4·06 m
7	1,1′	2·11 s	7·6—7·0 m	4·60 m	4·32 m	4·32 m	4·60 m	—
3-Br	1,2	—		—	—	—	—	—
	1,3	2·39 s		5·19 m	—	4·89 m	4·89 m	4·05 s
8	1,1′	2·15 s	7·5—6·8 m	4·60 m	4·35 m	4·35 m	4·60 m	—
4-OCH_3[c]	1,2	—		—	—	—	—	—
	1,3	2·43 s		5·19 m	—	4·89 m	4·89 m	4·07 s
9		2·62 s	7·8—7·0 m	4·70 t	4·42 t	4·42 t	4·70 t	4·08 t
3-OCH_3[d]								
10	1,1′	2·09 s	7·7—7·3 m	4·63 m	4·34 m	4·34 m	4·63 m	—
3-CF_3	1,2	—		—	—	—	—	—
	1,3	2·40 s		5·25 m	—	4·93 m	4·93 m	4·04 s
11	1,1′	2·05 s	7·4—6·9 m	4·54 m	4·23 m	4·23 m	4·54 m	—
3,4-$(CH_3)_2$[e]	1,2	2·17 s		—	4·74 m	—	—	4·12 s
	1,3	2·35 s		5·16 m	—	4·83 m	4·83 m	3·98 s

TABLE II
(*Continued*)

Compound	—$COCH_3$		Aryl	Ferrocenyl				
				$H_{2\,2'}$	$H_{3\,3'}$	$H_{4\,4'}$	$H_{5\,5'}$	C_5H_5
12	1,1′	2·03 s	7·2—6·8 m	4·55 m	4·23 m	4·23 m	4·55 m	—
3,5-$(CH_3)_2$[f]	1,2	2·28 s		—	4·74 m	—	—	4·13 s
	1,3	2·28 s		5·17 m	—	4·83 m	4·83 m	3·98 s
13	1,1′	2·13 s	7·6—7·0 m	4·65 m	4·31 m	4·31 m	4·56 m	—
3,4-Cl	1,2	—		—	—	—	—	—
	1,3	2·40 s		5·16 m	—	4·88 m	4·88 m	4·03 s
14	1,1′	2·14 s	7·7—7·2 m	4·59 m	4·35 m	4·35 m	4·59 m	—
3-CF_3, 4-Cl	1,2	2·28 s		—	—	—	—	4·15 s
	1,3	2·43 s		5·23 m	—	4·93 m	4·93 m	4·05 s
15	1,1′	2·07 s	8·1—7·2 m	4·65 t	4·30 m	4·30 m	4·56 t	
4-$COOC_2H_5$[g]	1,2	—		4·66 t	4·35 m	4·35 m	4·66 t	—
	1,3	2·41 s		—	—	—	—	—
				5·28 m	—	4·95 m	4·95 m	4·02 s
16	1,1′	2·08 s	7·6—6·8 m	4·58 m	4·29 m	4·29 m	4·58 m	—
4-$OCOCH_3$[h]	1,2	2·25 s		—	4·76 m	—	—	4·16 s
	1,3	2·39 s		5·18 m	—	4·86 m	4·86 m	4·03 s

[a] CH_3 2·33 s; [b] CH_3 2·40 s; [c] OCH_3 3·83 s; [d] OCH_3 3·98 s; [e] CH_3 2·22 s; [f] CH_3 2·28 s; [g] CH_2 4·36 kv; CH_3 1·37 t; [h] CH_3 2·25 s.

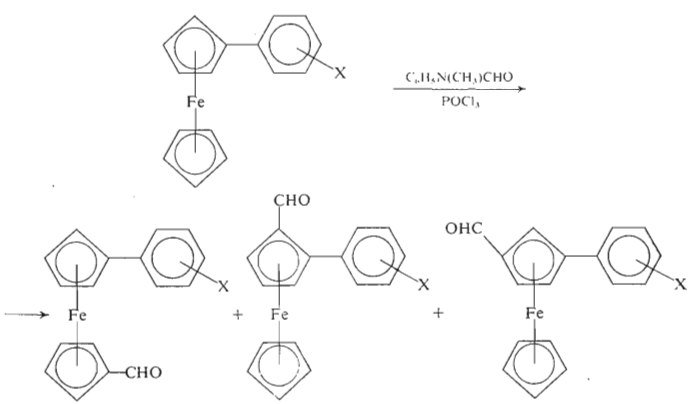
then 2 h at 65—70°C. On cooling to 0°C it was treated with sodium acetate (0·085 mol) in 70 ml of water. The system was stirred overnight, then extracted with ether. The combined ethereal extracts were washed with water, 1M-HCl, water, aqueous Na_2CO_3 and water. (The solutions were saturated with NaCl). After drying (Na_2SO_4) and distilling off the solvent the residue was chromatographed on a column of silica gel with benzene as eluent. Attempts at crystallization were not successful. The results are reviewed in Table III, the chemical shifts are given in Table IV.

RESULTS AND DISCUSSION

The formylation of arylferrocenes was conducted under the conditions of the Vielsmeyer–Haack reaction. In chromatography the formyl derivatives migrated as one band. The ^{1}H-NMR spectra of the dry residues exhibited three singlets in the region 9·75—10·25δ, associated with protons of three unequal —CHO groups. Our

assumption that these belonged to the three possible isomers (1,2-, 1,3- and 1,1'-) was confirmed by chemical shifts of the cyclopentadienyl protons of ferrocene (4·0 to 5·4δ), where two five-proton singlets of different non-substituted cyclopentadienyl rings were observed, and by multiplets belonging to protons of two different monosubstituted cyclopentadienyl rings. Attempts to resolve these mixtures by repeated chromatography under different conditions ended in failure.

In determining the relative contents of the individual isomers we proceeded from two assumptions: *1.* Slocum[6,7] has demonstrated that the α-protons (positions 2 and 5) of a monosubstituted cyclopentadienyl ring of a ferrocene are always deshielded more than the β-protons (positions 3 and 4) if the substituent is an electron-withdrawing one. Since the α-protons of phenylferrocene absorb at a lower field than the β-protons and the chemical shift is more or less related to the electron density on the given carbon atom we assumed that the proton signal of the formyl group in position 2 or 5 in respect to phenyl in phenylferrocene (α-formyl derivative) would also occur at a lower field. *2.* We assumed that even in our instance the disubstituted derivatives would be eluted in the order 1,2-, 1,1'- and 1,3-, as was the case with simpler derivatives[8] and acetyl derivatives of phenylferrocene[1].



SCHEME 1

After formylation of *p*-tolylferrocene (Scheme 1) the reaction mixture was chromatographed. The apparently non-composed band was resolved into 15 fractions that were taken to dryness and investigated for their ^{1}H-NMR spectra. The spectrum

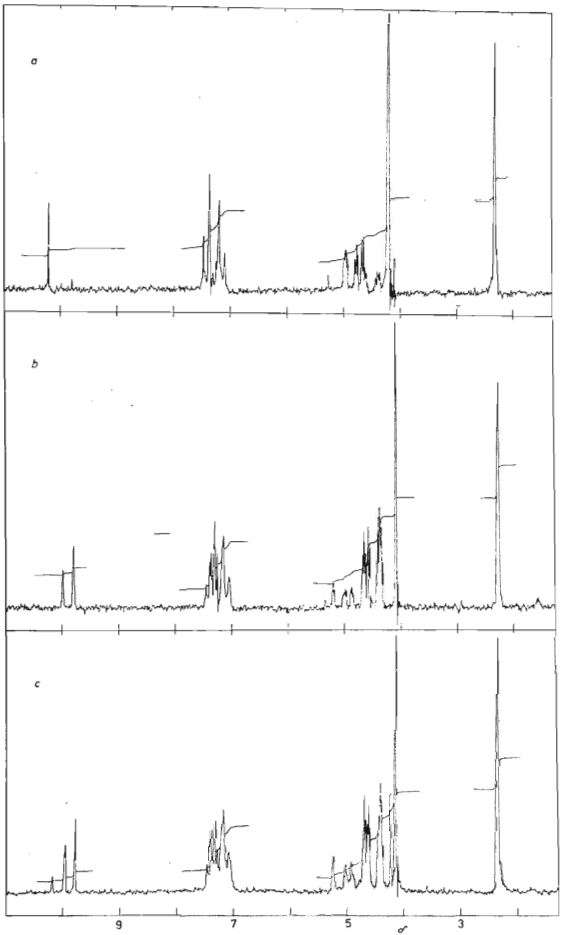


FIG. 1

^{1}N-NMR Spectra

a 2-(*p*-Tolyl)ferrocenecarbaldehyde; *b* mixture of 3-(*p*-tolyl)-ferrocenecarbaldehyde and

of the first one (Fig. 1, spectrum *a*) identified it as a single product; the other fractions proved to be bicomponent mixtures. (Spectrum *b* belongs to fraction 11). If our second assumption is correct the first fraction is practically the pure 1,2-isomer. Analysis of spectrum *a* and its comparison with spectrum *b* reveal that the chemical shift of the formyl group proton of the 1,2-derivative occurred at 10·18δ and the chemical shift of the nonsubstituted cyclopentadienyl ring of the same derivative at 4·23δ. With the 1,3-derivative the analogous chemical shifts were observed at 9·98δ and 4·14δ. The formyl group protons of the 1,1'-derivative exhibited a chemical shift at 9·79δ. Comparison of the spectra further reveals that the three one-proton multiplets at 5·25δ, 5·00δ and 4·95δ are characteristic of protons of the 1,3-disubstituted cyclopentadienyl ring. Characteristic of all 1,3-diformyl derivatives of the other arylferrocenes were three one-proton multiplets, occurring at a lower field than the cyclopentadienyl proton chemical shifts of the corresponding 1,2-derivatives. The chemical shifts of protons of the disubstituted cyclopentadienyl ring of a 1,2-derivative are usually difficult to read off exactly since they are partially overlapped by signals of the other derivatives. In a 1,1'-derivative the absorption by α-protons of the cyclopentadienyl ring attached to the aryl manifests itself as an apparent triplet at 4·62δ and that by α-protons of the formylated ring as an apparent triplet at 4·70δ; β-protons of the cyclopentadienyl rings form a multiplet with a centre at 4·4δ.

The relative contents of the individual isomers (1,2-, 1,3- and 1,1'-) were determined from integrated intensities of the aldehydic proton signals, and the results (Table III), especially the proportion of the 1,2 and 1,3 isomers, were verified by measuring the integrated intensities of protons of the non-substituted cyclopentadienyl ring (Fig. 1, spectrum *c*). As is seen, substitution in the aryl ring had practically no effect on the relative contents of the individual isomers. An exception was 3-methoxyphenylferrocene. The ^{1}H-NMR spectrum of its formyl derivative shows that the electrophilic substitution occurred on benzene, and not on ferrocene, since the chemical shifts of the ferrocenyl protons are similar to those of the starting compound. The benzene ring of 3-methoxyphenylferrocene binds two substituents with marked electron-releasing properties, *viz.* ferrocenyl and methoxyl, having simmilar effects on further substitution; an electrophilic particle will enter a *para* position in respect to either ferrocenyl or methoxyl. We suppose that substitution occurred in *para* position in respect to ferrocenyl. If it had occurred in the *ortho* position the part of spectrum belonging to the cyclopentadienyl ring protons would probably be different from that of the starting compound, due to a steric effect. The chemical shift of the CH_3O-group was observed at a much lower field than in the starting compound, which indicates an *ortho*-directing effect of the electron-withdrawing group $-CHO$.

1'-(*p*-tolyl)ferrocenecarbaldehyde; *c* mixture of 2-(*p*-tolyl)ferrocenecarbaldehyde, 3-(*p*-tolyl)-ferrocenecarbaldehyde and 1'-(*p*-tolyl)ferrocenecarbaldehyde.

TABLE III

Analytical Data of Formylated Arylferrocenes

Compound	Formula (m.v.)	Calculated % Fe	Yield	Derivatives, %		
				1,1′-	1,2-	1,3-
17 H	$C_{17}H_{14}FeO$ (290·2)	19·25 18·62	41	67	3	30
18 4-CH_3	$C_{18}H_{16}FeO$ (304·2)	18·36 17·75	53	54	8	38
19 3-CH_3	$C_{18}H_{16}FeO$ (304·2)	18·36 17·96	47	51	16	33
20 4-Cl	$C_{17}H_{13}ClFeO$ (324·6)	17·21 16·20	87	57	12	31
21 3-Cl	$C_{17}H_{13}ClFeO$ (324·6)	17·21 16·71	61	67	11	22
22 4-Br	$C_{17}H_{13}BrFeO$ (369·1)	15·13 14·64	45	67	9	24
23 3-Br	$C_{17}H_{13}BrFeO$ (369·1)	15·13 14·52	74	61	9	30
24 4-OCH_3	$C_{18}H_{16}FeO_2$ (320·2)	17·44 17·27	80	70	—	30
25[a] 3-OCH_3	$C_{18}H_{16}FeO_2$ (320·2)	17·44 17·38	45	—	—	—
26 3-CF_3	$C_{18}H_{13}F_3FeO$ (358·2)	15·99 14·95	58	59	10	31
27 3,4-$(CH_3)_2$	$C_{19}H_{18}FeO$ (318·2)	17·56 17·06	68	58	15	27
28 3,5-$(CH_3)_2$	$C_{19}H_{18}FeO$ (318·2)	17·56 16·88	74	52	15	33
29 3,4-Cl_2	$C_{17}H_{12}Cl_2FeO$ (359·9)	15·52 15·08	36	64	11	25
30 3-CF_3, 4-Cl	$C_{18}H_{12}ClF_3FeO$ (372·2)	15·03 14·03	68	60	14	26

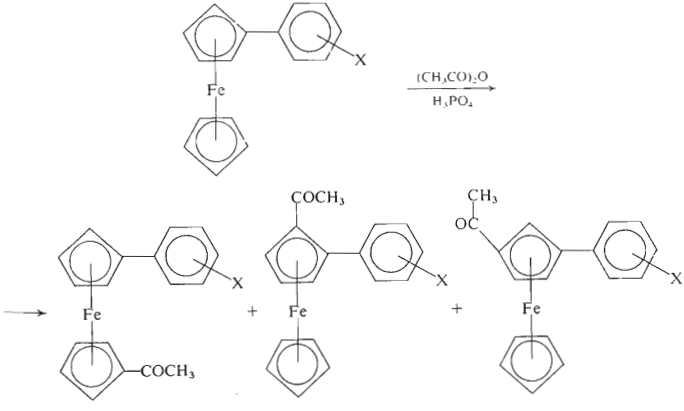
TABLE III
(*Continued*)

Compound	Formula (m.v.)	Calculated % Fe	Yield	Derivatives, %		
				1,1′-	1,2-	1,3-
31 4-C_2H_5	$C_{19}H_{18}FeO$ (318·2)	17·56 17·00	43	56	15	29
32 3-C_2H_5	$C_{19}H_{18}FeO$ (318·2)	17·56 17·26	14	52	16	32
33 4-$COOC_2H_5$	$C_{20}H_{18}FeO_3$ (362·2)	15·57 15·00	86	60	13	27

[a] Compound 25 was formylated in the benzene ring.

Formylation of *p*-dimethylaminophenylferrocene and *p*-cyanophenylferrocene failed to occur.

The prepared mixtures of formylated arylferrocenes spontaneously decomposed, especially if they were oils. Their condensation products with acetophenone and/or 1,3-indanedione were separated and fully characterized[9].



SCHEME 2

TABLE IV

^{1}H-NMR Chemical Shifts of Formylated Phenylferrocenes

Compound		—CHO	Aryl		
				H_2	H_3
17	1,1′	9·79 s	7·6—7·1 m	4·63 t	4·38 t
H	1,2	10·19 s		—	4·98 m
	1,3	9·99 s	5	5·25 m	—
18	1,1′	9·79 s	7·5—7·0 m	4·63 t	4·38 t
4-CH_3[a]	1,2	10·18 s		—	—
	1,3	9·98 s		5·23 m	—
19	1,1′	9·80 s	7·4—7·0 m	4·64 t	4·44 m
3-CH_3[b]	1,2	10·26 s		—	—
	1,3	9·99 s		5·25 m	—
20	1,1′	9·79 s	7·5—7·1 m	4·63 t	4·43 m
4-Cl	1,2	10·14 s		—	—
	1,3	9·98 s		5·22 m	—
21	1,1′	9·81 s	7·7—7·0	4·64 t	4·34 t
3-Cl	1,2	10·10 s		—	—
	1,3	9·91 s		5·25 m	—
22	1,1′	9·79 s	7·6—7·1 m	4·60 t	4·40 m
4-Br	1,2	10·14 s		—	—
	1,3	9·98 s		5·20 m	—
23	1,1′	9·77 s	7·7—7·0 m	4·65 m	4·40 m
3-Br	1,2	10·13 s		—	—
	1-3	9·95 s		5·20 m	—
24	1,1′	9·80 s	7·5—6·7 m	4·63 t	4·37 t
4-OCH_3[c]	1,2	—		—	—
	1,3	9·98 s		5·19 m	—
25		10·40 s	7·8—7·0 m	4·70 t	4·42 t
3-OCH_3[d]					
26	1,1′	9·80 s	7·7—7·2 m	4·64 t	4·74 m
3-CF_3	1,2	10·13 s		—	—
	1,3	9·99 s		5·29 m	—
27	1,1′	9·79 s	7·4—6·9 m	4·59 t	4·33 t
3,4-$(CH_3)_2$[e]	1,2	10·19 s		—	—
	1,3	9·95 s		9·15 m	—

TABLE IV
(*Continued*)

Ferrocenyl						
H_4	H_5	$H_{2'}$	$H_{3'}$	$H_{4'}$	$H_{5'}$	C_5H_5
4·38 t	4·63 m	4·73 t	4·44 t	4·44 t	4·73 t	—
4·68 m	4·78 m	—	—	—	—	4·23 s
5·03 m	4·94 m	—	—	—	—	4·14 s
4·38 t	4·63 t	4·70 t	4·44 t	4·44 t	4·70 t	—
—	—	—	—	—	—	4·23 s
5·01 m	4·93 m	—	—	—	—	4·15 s
4·44 m	4·64 t	4·73 t	4·44 m	4·44 m	4·73 t	—
—	—	—	—	—	—	4·24 s
5·03 m	4·93 m	—	—	—	—	4·15 s
4·43 m	4·63 t	4·69 t	4·43 m	4·43 m	4·69 t	—
—	—	—	—	—	—	4·23 s
5·00 m	4·95 m	—	—	—	—	4·14 s
4·34 t	4·64 t	4·76 t	4·44 t	4·44 t	4·76 t	—
—	—	—	—	—	—	3·21 s
5·05 m	4·99 m	—	—	—	—	4·14 s
4·40 m	4·60 t	4·67 t	4·40 m	4·40 m	4·67 t	—
—	—	—	—	—	—	4·23 s
4·98 m	4·93 m	—	—	—	—	4·17 s
4·40 m	4·65 m	4·65 m	4·40 m	4·40 m	4·65 m	—
—	—	—	—	—	—	4·20 s
4·97 m	4·97 m	—	—	—	—	4·11 s
4·37 t	4·63 t	4·67 t	4·44 t	4·44 t	4·67 t	—
—	—	—	—	—	—	—
4·99 m	4·91 m	—	—	—	—	4·15 s
4·42 t	4·70 t	—	—	—	—	4·08 s
4·74 m	4·64 t	4·75 t	4·47 m	4·47 m	4·75 t	—
—	—	—	—	—	—	4·24 s
5·05 m	4·98 m	—	—	—	—	4·16 s
4·33 t	4·59 t	4·66 t	4·39 t	4·39 t	4·66 t	—
—	—	—	—	—	—	4·22 s
4·98 m	4·48 m	—	—	—	—	4·10 s

TABLE IV
(*Continued*)

Compound		—CHO	Aryl		
				H_2	H_3
28	1,1′	9·78 s	7·2—6·8 m	4·57 t	4·30 t
3,5-$(CH_3)_2$[f]	1,2	10·20 s		—	—
	1,3	9·95 s		5·18 m	—
29	1,1′	9·79 s	7·7—7·0 m	4·61 t	4·41 t
3,4-Cl_2	1,2	10·13 s		—	—
	1,3	9·98 s		5·19 m	—
30	1,1′	9·80 s	7·9—7·1 m	4·62 t	4·44 m
3-CH_3, 4-Cl	1,2	10·11 s		—	—
	1,3	9·99 s		5·24 m	—
31	1,1′	9·78 s	7·5—7·0 m	4·60 t	4·38 m
4-C_2H_5[g]	1,2	10·18 s		—	—
	1,3	9·69 s		5·20 m	—
32	1,1′	9·80 s	7·5—6·9 m	4·63 t	4·43 m
3-C_2H_5[h]	1,2	10·20 s		—	—
	1,3	9·99 s		5·25 m	—
33	1,1′	9·78 s	8·0—7·0 m	4·58 t	4·39 m
4-$COOC_2H_5$[i]	1,2	10·18 s		—	—
	1,3	10·00 s		5·30 m	—

Since acetic anhydride is a milder agent than Perier's complex the reaction mixtures should be easier to analyse (Scheme 2). Table IV shows that this expectation was partially fulfilled. With the exception of 3-methoxyphenylferrocene no substitution took place in the benzene ring and minimum amounts of 1,2-isomers were formed. Employing Perier's complex Rosenblum[1] obtained products with acetyls in the benzene ring and a considerable quantity of 1,2-isomers. As can be seen from Table IV, neither formylation nor acetylation was markedly affected by a substituent as to the proportion of the isomers. Compared to formylation, acetylation to position 1′ occurred to a greater extent. In the 4-hydroxyphenyl derivative the hydroxyl group was acetylated too. Acetylation of 3-methoxyphenylferrocene occurred

TABLE IV
(*Continued*)

Ferrocenyl						
H_4	H_5	$H_{2'}$	$H_{3'}$	$H_{4'}$	$H_{5'}$	C_5H_5
4·30 t	4·57 t	4·64 t	4·36 t	4·36 t	4·64 t	—
—	—	—	—	—	—	4·14 s
4·96 m	4·86 m	—	—	—	—	4·07 s
4·41 m	4·61 t	4·65 t	4·41 m	4·41 m	4·65 m	—
—	—	—	—	—	—	4·21 s
4·95 m	4·95 m	—	—	—	—	4·12 s
4·44 m	4·62 t	4·70 t	4·44 m	4·44 m	4·70 t	—
—	—	—	—	—	—	4·22 s
4·98 m	4·98 m	—	—	—	—	4·13 s
4·38 m	4·60 t	4·67 t	4·38 m	4·38 m	4·67 t	—
—	—	—	—	—	—	4·22 s
4·99 m	4·89 m	—	—	—	—	4·10 s
4·43 m	4·63 t	4·67 t	4·43 m	4·43 m	4·76 t	—
—	—	—	—	—	—	4·24 s
5·04 m	4·91 m	—	—	—	—	4·14 s
4·39 m	4·58 t	4·75 t	4·39 m	4·39 m	4·75 t	—
—	—	—	—	—	—	4·20 s
5·12 m	4·96 m	—	—	—	—	4·09 s

[a] CH_3 2·34 s; [b] CH_3 2·38 s; [c] $—OCH_3$ 3·79 s; [d] OCH_3 3·98 s; [e] CH_3 2·25 s, 2·20 s; [f] CH_3 2·30 s; [g] CH_2 2·61 kv, CH_3 1·23 t; [h] CH_2 2·66 kv, CH_3 1·27 t; [i] CH_3 1·37 t.

in the benzene ring in *para* position to ferrocenyl, as did its formylation. The relative contents of the individual acetyl derivatives were determined as in the case of formylation. With acetylated arylferrocenes the signal associated with the acetyl group protons of the 1,1'-derivatives was observed at the highest field ($\delta \sim 2{\cdot}15$). The acetyl group of the 1,3-derivative absorbed at about 2·4δ. It has proved characteristic of the 1,3-derivatives that protons of a disubstituted cyclopentadienyl ring absorb as two multiplets, in a ratio of 2 : 1. In the 1,2-derivative the acetyl group absorb at approximately 2·30δ, which was corroborated by chromatographical separation of acetylphenylferrocenes and by comparison by their properties with Rosenblum's data[1].

Our observation in both formylation and acetylation of arylferrocenes that apart from the 1,1'-isomer the relative content of the 1,3-isomer strongly prevailed over that of the 1,2-isomer (formed to a negligible extent only) is at variance with Rosenblum's results. Rosenblum acetylated phenylferrocene with Perier's complex and found that the amount of the 1,2 isomer exceeded that of the 1,3-isomer. Since the latest studies[10–12] prove that the resonance effects of substituents are transmitted equally to positions 2,5 and 3,4 our results can be interpreted in terms of steric requirements of the aryl and the electrophilic agent. The agents we used, *i.e.* protonized acetic anhydride and a complex of N-methylformanilide with $POCl_3$, are bulkier than Perier's complex. The high reactivity of ferrocene with electrophilic agents allows us to assume that the actual acetylating agent was protonized acetic anhydride, and not acetylium cations, produced by dissociation.

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