

## ARYLATION OF FERROCENE DERIVATIVES

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Arylation of acetylferrocene, 1,1'-diacetylferrocene, ferrocenecarbaldehyde, and 1-ferrocenyl-2-phenylethylene with various diazonium salts has been examined. Depending on the diazonium salt, the experiments have furnished either arylation products of the ferrocene derivative or coupling products (in some cases arylation and coupling products) of fulvenes arisen by degradation of the ferrocene derivative. The structure of products was determined by means of PMR spectra and, with some fulvene derivatives, also by mass spectra.

The arylation of ferrocene has been paid considerable attention<sup>1,2</sup> but the reports on arylation of ferrocene derivatives are rather rare. Thus, arylation of methyl- and ethylferrocene with benzenediazonium chloride affording in a low yield a mixture of monoarylated and polyarylated products has been described by Nesmejanov and coworkers<sup>3</sup>. Small yields of arylation products have been obtained from acetylferrocene, methoxycarbonylferrocene, and 1,1'-bis(methoxycarbonyl)ferrocene by arylation with *p*-nitrobenzenediazonium chloride<sup>3</sup>. The attempted arylation of 1,1'-diacylferrocenes gave iron-free products<sup>3-6</sup> which were assigned the structure of 6-hydroxy-6-alkyl(aryl)-2-phenylazofulvene by Bozak and Rinehart<sup>6</sup>. The arylation of nitroferrocene failed<sup>6</sup>.

The aim of the present work was to examine the influence of arylation conditions as well as the effect of substituents on the benzene ring of diazonium salts on arylations of acetylferrocene, 1,1'-diacetylferrocene, ferrocenecarbaldehyde, and 1-ferrocenyl-2-arylethylene.

## EXPERIMENTAL

PMR spectra were measured in 4–7% CDCl<sub>3</sub> solutions (99.5% of the D isotope) on a Tesla BS 487 A apparatus (80 MHz) with the use of tetramethylsilane as internal standard. Chemical shifts and coupling constants were measured at 23°C with the accuracy of ±0.2 Hz and ±0.4 Hz, resp., and summarised in Tables I and II.

Mass spectra were determined by the direct inlet technique on a MS 902 S apparatus at the ionic source temperature of about 120°C, electron energy 70 eV (trap current) 100 μA. Exact mass measurements were performed with the discrimination of about 25000–10% valley definition (heptacosafuorotributylamine as reference standard).

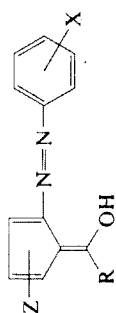


TABLE I  
PMR Chemical Shifts of 6-Hydroxyfulvene Derivatives

Compound <sup>a</sup>	4	5	3	R	OH	arom.	J <sub>4,5</sub>	J <sub>3,4</sub>	J <sub>3,5</sub>
I R = CH <sub>3</sub> , X = 4-Br, Z = 3-(3-BrC <sub>6</sub> H <sub>4</sub> )	6.51 (d)	6.95 (d)	—	2.07 (s)	15.20 (s)	7.45 (m/8 H)	—	3.3	2.0
II R = CH <sub>3</sub> , X = 4-Br, Z = H	6.55 (qua)	6.97 (qua)	7.68 (t)	2.54 (s)	15.00 (s)	7.43 (d/4 H)	5	4	2.4
III R = CH <sub>3</sub> , X = 4-Cl, Z = H	6.53 (qua)	6.96 (qua)	7.61 (qui)	2.53 (s)	15.04 (s)	7.38 (d/4 H)	4.9	3.3	2.0
IV R = CH <sub>3</sub> , X = 3-NO <sub>2</sub> , Z = H	6.60 (qua)	6.98 (qua)	7.66 (m)	2.56 (s)	15.00 (s)	8.33 (t/1 H) 7.5—8.0 (m, 3 H)	4.9	3.2	2.0
V R = CH <sub>3</sub> , X = 3-NO <sub>2</sub> , Z = 3-(3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> )	6.60 (d)	7.03 (d)	—	2.06 (s)	15.33 (s)	8.37 (t/1 H) 8.27 (t/1 H) 7.5—8.0 (m/6 H)	5	—	—
XIV R = H, X = 4-Br, Z = 3-(4-BrC <sub>6</sub> H <sub>4</sub> )	6.98 (d)	7.15 (d)	—	9.44 (s)	14.78 (s)	7.45 (m, 8 H)	5	—	—
XV R = H, X = 4-Br, Z = H	6.65 (qua)	7.10 (qua)	7.68 (t)	9.43 (s)	14.58 (s)	7.46 (d, 4 H)	4	3	2
XVI R = H, X = 4-Br, Z = 5-(4-BrC <sub>6</sub> H <sub>4</sub> )	6.80 (d)	—	7.68 (d)	9.42 (s)	14.61 (s)	7.42 (d, 4 H)	—	3.1	—
XIX R = CH <sub>3</sub> , H = 4-NO <sub>2</sub> , Z = H	6.65 (qua)	6.97 (qua)	7.75 (m)	2.58 (s)	14.00 (s)	7.53 (d, 2 H) 8.50 (d, 2 H) (J <sub>AB</sub> 9.0)	5	3	2

<sup>a</sup> s, singlet; d, doublet; t, triplet; qua, quartet; qui, quintet; m, multiplet.

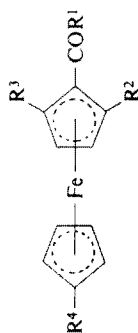


TABLE II  
PMR Chemical Shifts of Arylated Acylferrocenes

Compound	CH <sub>3</sub>	3·4	2·5	3'4'	2'5'	C <sub>5</sub> H <sub>5</sub>	ar.
<i>VI</i> R <sup>1</sup> = CH <sub>3</sub> , R <sup>2</sup> = R <sup>3</sup> = H, R <sup>4</sup> = 3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	2·15 (s)	4·38 (t)	4·66 (t)	4·47 (t)	4·74 (t)	—	7·50 (d) 8·00 (d)
<i>IX</i> R <sup>1</sup> = CH <sub>3</sub> , R <sup>2</sup> = 4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> , R <sup>3</sup> = R <sup>4</sup> = H	2·24 (s)	4·86 (s)	—	—	—	4·27 (s)	4·64 (d) 8·20 (d)
<i>X</i> R <sup>1</sup> = CH <sub>3</sub> , R <sup>2</sup> = 4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> , R <sup>3</sup> = R <sup>4</sup> = H	2·45 (s)	4·9 (t) 4·69 (d)	4·76 (t)	—	—	4·25 (s)	7·70 (d) 8·15 (d)
<i>XII</i> R <sup>1</sup> = CH <sub>3</sub> , R <sup>2</sup> = R <sup>3</sup> = H, R <sup>4</sup> = 4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	2·15 (s)	4·38 (t)	4·64 (t)	4·50 (t)	4·75 (t)	—	7·52 (d) 9·18 (d)
<i>XVII</i> R <sup>1</sup> = R <sup>3</sup> = R <sup>4</sup> = H, R <sup>2</sup> = 4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> , CHO	10·17 (s)	4·97 (t) 4·82 (d)	5·07 (t)	—	—	4·29 (s)	7·70 (d) 8·20 (d)
<i>XVIII</i> R <sup>1</sup> = R <sup>2</sup> = R <sup>3</sup> = H, R <sup>4</sup> = 4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> , CHO	9·8 (s)	4·60 (t)	4·84 (t)	4·50 (t)	4·66 (t)	—	7·55 (d) 8·17 (d)

*Melting points* were taken on a heated microscope stage (Kofler apparatus). Yields of products are expressed as evaporation residue of particular bands after the chromatography and refer to the starting ferrocene derivative. Some crystallisations (especially those of the bromo derivatives) were accompanied by considerable losses.

#### Arylation of Acetylferrocene with *p*-Bromobenzenediazonium Salts

*Method A.* A solution of *p*-bromobenzenediazonium sulfate previously prepared by diazotisation of *p*-bromoaniline (6.8 g; 0.05 mol) in 20% aqueous sulfuric acid (100 ml) by the action of sodium nitrite (3.5 g; 0.05 mol), was added to a stirred mixture consisting of acetylferrocene (4.56 g; 0.02 mol) in dichloromethane (100 ml) and sodium acetate trihydrate (20 g) in water (200 ml). The whole reaction mixture was stirred at room temperature for 20 h, treated with sodium hydrogen sulfite (to reduce the ferricenium salt), and extracted repeatedly with dichloromethane. The extracts were combined, washed with water, dried over anhydrous sodium sulfate, and evaporated under diminished pressure. The residue was chromatographed on a column of silica gel (Kavalier Glassworks, Votice, Czechoslovakia) with the use of the benzene-hexane mixture as eluant. Three of the several bands afforded the following products. The first band yielded 0.63 g (7.1%) of 6-hydroxy-6-methyl-3-(*p*-bromophenyl)-2-(*p*-bromophenylazo)fulvene (*I*) as deep red crystals, m.p. 151–153°C (after crystallisation from benzene) and 157°C (methanol). For  $C_{19}H_{14}Br_2N_2O$  (446.1) ( $M^+$  446) calculated: 6.60% N, 35.80% Br; found: 6.29% N, 35.26% Br. The second band yielded 0.75 g (13%) of 6-hydroxy-6-methyl-2-(*p*-bromophenylazo)fulvene (*II*) as brownish red crystals, m.p. 118–120°C (benzene-heptane). For  $C_{13}H_{11}BrN_2O$  (291.1) ( $M^+$  290) calculated: 9.65% N, 27.44% Br; found: 9.81% N, 28.03% Br. The third band (elution with benzene) yielded 1.8 g (39%) of the starting acetylferrocene.

*Method B.* To a stirred solution of acetylferrocene (2.28 g; 0.01 mol) in acetic acid (25 ml) there was added dropwise over one hour a solution of *p*-bromobenzenediazonium sulfate previously prepared from 3.4 g (0.02 mol) of *p*-bromoaniline. The whole reaction mixture was then stirred for one hour at room temperature and for 2 h at 45–50°C, poured into ice-cold water, treated with sodium hydrogen sulfite, and extracted with dichloromethane. The extracts were processed analogously to method *A*. Yields, 0.22 g (5%) of compound *I*, 0.25 g (11.7%) of compound *II*, and 0.32 g (40.3%) of acetylferrocene.

*Method C.* A solution of *p*-bromobenzenediazonium fluoroborate (2.6 g; 0.01 mol) in dimethyl sulfoxide (25 ml; nitrogen was previously passed through this solvent) was added dropwise at 20°C into a stirred solution of acetylferrocene (2.28 g; 0.01 mol) and tetraethylammonium hydroxide (4.41 g; 0.03 mol) in dimethyl sulfoxide (75 ml) over 10 min. The whole reaction mixture was then stirred for additional one hour, poured into water, and extracted with ether. The ethereal layers were combined, washed with water, and dried over anhydrous sodium sulfate. The ether was evaporated and the residue chromatographed on a column of silica gel to afford 0.35 g (7.3%) of compound *I*, 0.32 g (11.2%) of compound *II*, and 0.75 g (32.8%) of the starting acetylferrocene.

#### Arylation of Acetylferrocene with *p*-Chlorobenzenediazonium Sulfate

Acetylferrocene (3.42 g; 0.015 mol) and *p*-chloroaniline (1.29 g; 0.02 mol) were processed analogously to method *A* to afford 0.34 g (9.3%) of 6-hydroxy-6-methyl-2-(*p*-chlorophenylazo)fulvene (*III*) as red crystals, m.p. 117–119°C (benzene-heptane). In addition to compound *III*, another two compounds (traces) and the unreacted acetylferrocene were isolated. For  $C_{13}H_{11}ClN_2O$  (246.6) calculated: 11.36% N, 14.37% Cl; found: 11.28% N, 14.34% Cl.

In the attempted arylation of acetylferrocene with benzenediazonium sulfate and *p*-methylbenzenediazonium sulfate by method *A*, there were isolated (in addition to the unreacted acetylferrocene) two substances of  $R_F$  values and colour similar to those of compounds *I* and *II*, but their quantity was too small to allow a more detailed characterisation.

#### Arylation of Acetylferrocene with *m*-Nitrobenzenediazonium Sulfate

The reaction was performed by method *B* from acetylferrocene (6.84 g; 0.03 mol) and *m*-nitroaniline (8.4 g; 0.06 mol). The column chromatography was effected on silica gel with 97 : 3 benzene-ethyl acetate as eluant (nine bands). The following compounds were successively eluted:

a) 0.54 g (7%) of 6-hydroxy-6-methyl-2-(*m*-nitrophenylazo)fulvene (*IV*) from band 2. Red crystals, m.p. 151–153°C (benzene). For  $C_{13}H_{11}N_3O_3$  (257.2) ( $M^+$  257) calculated: 16.42% N, 60.69% C, 4.36% H; found: 16.75% N, 60.54% C, 4.49% H.

b) 0.42 g (3.7%) of 6-hydroxy-6-methyl-3-(*m*-nitrophenyl)-2-(*m*-nitrophenylazo)fulvene (*V*) from band 3. Red crystals, m.p. 177–178°C (benzene and then methanol). For  $C_{19}H_{14}N_4O_5$  (378.3) ( $M^+$  378) calculated: 14.81% N, 60.31% C, 3.74% H; found: 14.93% N, 60.53% C, 3.87% H

c) 0.60 g (5.3%) of 6-hydroxy-6-methyl-5(?)-(*m*-nitrophenyl)-2-(*m*-nitrophenylazo)fulvene (*VI*) from band 5. Deep red crystals, m.p. 196–201°C (benzene). For  $C_{19}H_{14}N_4O_5$  (378.3) ( $M^+$  378) calculated: 14.81% N, 60.31% C, 3.74% H; found: 14.84% N, 60.23% C, 3.29% H. In view of the insolubility of compound *VI* both in deuteriochloroform and hexadeuteriodimethyl sulfoxide, the PMR spectrum was not measured.

d) 0.32 g (3.9%) of 1-acetyl-1'-(*m*-nitrophenyl)ferrocene (*VII*) from band 9. Brown crystals, m.p. 81–82°C (hexane). For  $C_{18}H_{15}FeNO_3$  (349.1) calculated: 15.99% Fe, 4.01% N; found: 15.68% Fe, 4.37% N.

#### Arylation of Acetylferrocene with *p*-Nitrobenzenediazonium Sulfate

The reaction was performed by method *B* from acetylferrocene (4.56 g; 0.02 mol) and *p*-nitroaniline (5.6 g; 0.04 mol). The following compounds were isolated by chromatography (14 bands):

a) 0.15 g of a highly insoluble material (*VIII*) from band 8. M.p. 250–252°C. The spectral measurement failed.

b) 0.1 g (0.8%) of 1-acetyl-2,5-bis(*p*-nitrophenyl)ferrocene (*IX*) from band 10. Red crystals, m.p. 172–175°C (benzene). For  $C_{24}H_{18}FeN_2O_5$  (470.2) calculated: 11.87% Fe, 5.95% N; found: 11.31% Fe, 5.48% N.

c) 0.47 g (6.7%) of 1-acetyl-2-(*p*-nitrophenyl)ferrocene (*X*) from band 11. M.p. 161–163°C (benzene); reported<sup>3</sup>, m.p. 158–160°C.

d) From band 12, there was obtained 0.22 g (3.8%) of a substance (m.p. 154–163°C after recrystallisation from benzene), which was shown by PMR spectroscopy to be a mixture of 1-acetyl-2-(*p*-nitrophenyl)ferrocene (*X*) and 1-acetyl-3-(*p*-nitrophenyl)ferrocene (*XI*) in the ratio of about 1 : 3. For  $C_{18}H_{15}FeNO_3$  (349.1) calculated: 15.99% Fe, 4.01% N; found: 15.73% Fe, 3.78% N.

e) Band 13 yielded 0.77 g (11%) of 1-acetyl-1'-(*p*-nitrophenyl)ferrocene (*XII*), m.p. 121–122°C (benzene); reported<sup>3</sup>, m.p. 122–123°C.

f) Band 14 yielded 0.1 g of a substance (m.p. 140–145°C after crystallisation from benzene) which was shown by PMR spectroscopy to represent a mixture of 1-acetyl-1',2-bis(*p*-nitrophenyl)-

1-acetyl-1',3-bis(*p*-nitrophenyl)-, and 1-acetyl-1',2,3-tris(*p*-nitrophenyl)ferrocene (*XIII*). Found: 10.26% Fe, 5.21% N.

#### Arylation of Ferrocenecarbaldehyde with *p*-Bromobenzenediazonium Sulfate

The reaction was performed by method *A* (see the arylation of acetylferrocene) from ferrocenecarbaldehyde (4.28 g; 0.02 mol) and *p*-bromoaniline (2.54 g; 0.02 mol). The following compounds were isolated by chromatography (four bands):

a) 0.25 g (2.9%) of 6-hydroxy-3-(*p*-bromophenyl)-2-(*p*-bromophenylazo)fulvene (*XIV*) as red crystals, m.p. 154–159°C (benzene–heptane). For  $C_{18}H_{11}Br_2N_2O$  (431.1) ( $M^+$  429) calculated: 37.03% Br, 6.49% N; found: 36.73% Br, 6.83% N.

b) 0.19 g (3.5%) of 6-hydroxy-2-(*p*-bromophenylazo)fulvene (*XV*), m.p. 82–88°C (benzene–heptane). For  $C_{12}H_9BrN_2O$  (277.1) calculated: 28.83% Br, 10.11% N; found: 29.37% Br, 10.07% N.

c) 0.12 g (1.4%) of 6-hydroxy-5-(*p*-bromophenyl)-2-(*p*-bromophenylazo)fulvene (*XVI*). Red needles, m.p. 188–189°C (benzene–heptane). For  $C_{18}H_{11}Br_2N_2O$  (431.1) ( $M^+$  429) calculated: 37.07% Br, 6.49% N; found: 37.24% Br, 6.81% N.

#### Attempted Arylation of Ferrocenecarbaldehyde with *p*-Nitrobenzenediazonium Sulfate

Method *A* (from 2.14 g *i.e.* 0.01 mol of ferrocenecarbaldehyde) afforded 16 chromatographic bands; no product was isolated in such a quantity to allow characterisation.

Method *B* (from 4.28 g *i.e.* 0.02 mol of ferrocenecarbaldehyde) afforded numerous products and polymers insoluble in benzene. By repeated chromatography, there was isolated 0.06 g (0.9%) of 2-*p*-nitrophenylferrocenecarbaldehyde (*XVII*), m.p. 146–147°C (benzene–heptane), and 0.05 g (0.07%) of a 1'-*p*-nitrophenylferrocenecarbaldehyde (*XVIII*), m.p. 140–145°C (decomp.) (benzene). For  $C_{17}H_{13}FeNO_3$  (335.1) calculated: 16.66% Fe, 4.17% N; found (*XVII*): 16.80% Fe; 4.29% N; found (*XVIII*): 16.93% Fe, 4.33% N.

#### Attempted Arylation of 1,1'-Diacetylferrocene with *p*-Nitrobenzenediazonium Chloride

With the use of method *B*, 1,1'-diacetylferrocene (2.7 g; 0.01 mol), and *p*-nitroaniline (7 g; 0.03 mol) there was obtained 0.71 g (14%) of 6-hydroxy-6-methyl-2-(*p*-nitrophenylazo)fulvene (*XIX*), m.p. 226°C (benzene); reported<sup>4</sup>, m.p. 202–203°C. Another chromatographic band yielded 0.06 g (0.8%) of 6-hydroxy-6-methyl-*X*-(*p*-nitrophenyl)-2-(*p*-nitrophenylazo)fulvene (*XX*), m.p. 300°C (benzene). For  $C_{19}H_{14}N_4O_5$  (378.3) calculated: 14.81% N, 60.31% C, 3.74% H; found: 14.69% N, 60.12% C, 3.92% H.

#### Attempted H-D Exchange

The 6-hydroxylic function of compounds *II* and *IV* was deuterated by heating the samples for several hours in  $D_2O$ -anhydrous tetrahydrofuran (compound *II*) or  $D_2O$ -deuteriochloroform (compound *IV*), drying over anhydrous sodium sulfate, evaporating the solvent, and crystallising the residue. As shown by mass spectra, the exchange occurred by about 40% only.

#### Attempted Decomposition of Acetylferrocene and Ferrocene in Acidic Media

A solution of ferrocene or acetylferrocene (1 g each) in dichloromethane was acidified with conc. sulfuric acid, stirred overnight, poured into water, treated with sodium hydrogen sulfite (to reduce

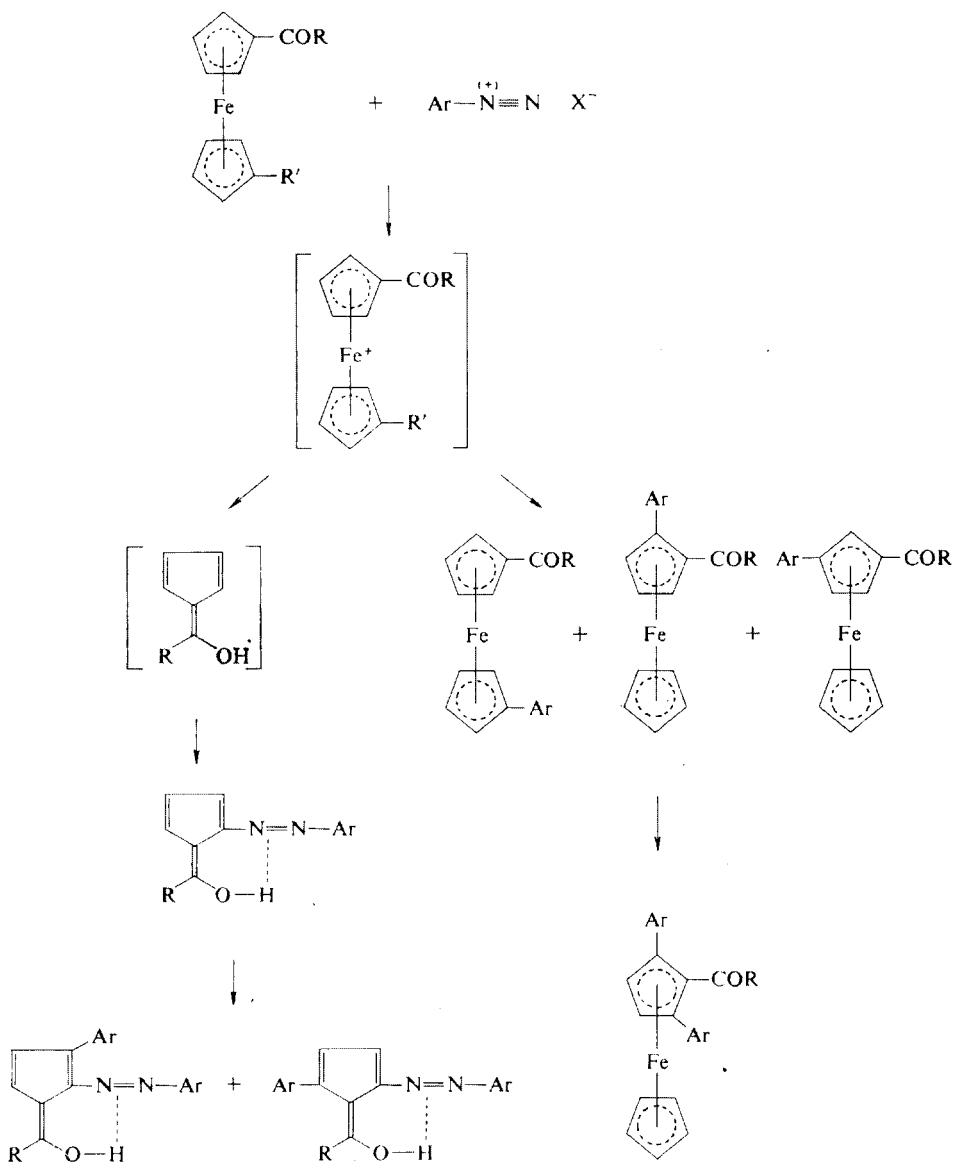
the ferricenium salts), and extracted with dichloromethane. The extracts were combined, washed with water, and evaporated to afford the unreacted ferrocene (0.85 g) and acetylferrocene (0.65 g).

## RESULTS AND DISCUSSION

On the basis of numerous successful arylations of ferrocene<sup>1,2</sup> as well as the successful arylation of acetylferrocene with *p*-nitrobenzenediazonium chloride it appeared of interest to attempt the preparation of some other 1'-substituted acetylferrocenes or ferrocenecarbaldehydes by this method. As shown by the successful arylation of 2-furancarbaldehyde<sup>7</sup> and 2-acetylfuran<sup>8</sup>, the presence of a carbonyl group does not interfere with the arylation. Arylations of compounds containing a double bond have also been reported<sup>9,10</sup>. We have observed, however, that the arylation of 1-ferrocenyl-2-phenylethylene fails under conditions of both the Gomberg-Bachmann and the Meerwein reactions. In spite of the neutral media, polymerisation predominated over the arylation.

It has been now observed in arylations of acetylferrocene that the reaction course does not practically depend on the reaction conditions since identical products are obtained both in acidic (acetic acid) and neutral (dichloromethane) media. On the other hand, however, the result of the reaction strongly depends on substituents of the benzene ring of diazonium salts. The action of sulfuric acid<sup>11</sup> or diazonium salts is assumed to result in two competitive reactions, namely, rupture of the bond between iron and the cyclopentadienyl residues and arylation. As established by Rinehart<sup>12,13</sup>, the substituents with electron-accepting properties weaken the bond between iron and the substituted cyclopentadiene ring in a ionisation chamber of a mass spectrometer. We have also observed that more acetylferrocene (35%) than ferrocene (15%) is decomposed in acidic media under otherwise identical conditions. The direction of the acetylferricenium cation reaction depends on the reactivity of the arylating radical. In the case of relatively poorly reactive radicals such as phenyl, *p*-tolyl, *p*-bromophenyl, and *p*-chlorophenyl radicals, the faster reaction was the conversion of acetylferrocene to 6-hydroxy-6-methylfulvene (or acetylcyclopentadiene) which then coupled with the diazonium salts present and was arylated with the formation of two isomeric aryl-arylazofulvenes. On the other hand, in the arylation with *p*-nitrobenzenediazonium sulfate (formation of a highly reactive *p*-nitrophenyl radical), only the mono-, bis-, and tris-arylated acetylferrocenes were isolated. It may be inferred from our experiments that the *m*-nitrophenyl is somewhat less reactive since there were isolated both the products of reactions with fulvene and the product of the acetylferrocene arylation.

The arylation of ferrocenecarbaldehyde with *p*-bromobenzediazonium sulfate was similar to that of acetylferrocene, *i.e.*, only the coupling and arylation products of 6-hydroxyfulvene were obtained. By the reaction of ferrocenecarbaldehyde with *p*-nitrobenzenediazonium sulfate numerous substances resulted from which trace



SCHEME 1

- A  $\text{R}' = \text{H}$ ,  $\text{R} = \text{CH}_3$ ,  $\text{Ar} = p\text{-Br}-\text{C}_6\text{H}_4$ ,  $p\text{-Cl}-\text{C}_6\text{H}_4$ ,  $m\text{-NO}_2-\text{C}_6\text{H}_4$   
 $\text{R}' = \text{H}$ ,  $\text{R} = \text{H}$ ,  $\text{Ar} = p\text{-Br}-\text{C}_6\text{H}_4$ ,  
 $\text{R}' = \text{COCH}_3$ ,  $\text{R} = \text{CH}_3$ ,  $\text{Ar} = p\text{-NO}_2-\text{C}_6\text{H}_4$
- B  $\text{R}' = \text{H}$ ,  $\text{R} = \text{CH}_3$ ,  $\text{Ar} = p\text{-NO}-\text{C}_6\text{H}_4$ ,  $m\text{-NO}_2-\text{C}_6\text{H}_4$   
 $\text{R}' = \text{H}$ ,  $\text{R} = \text{H}$ ,  $\text{Ar} = p\text{-NO}_2-\text{C}_6\text{H}_4$

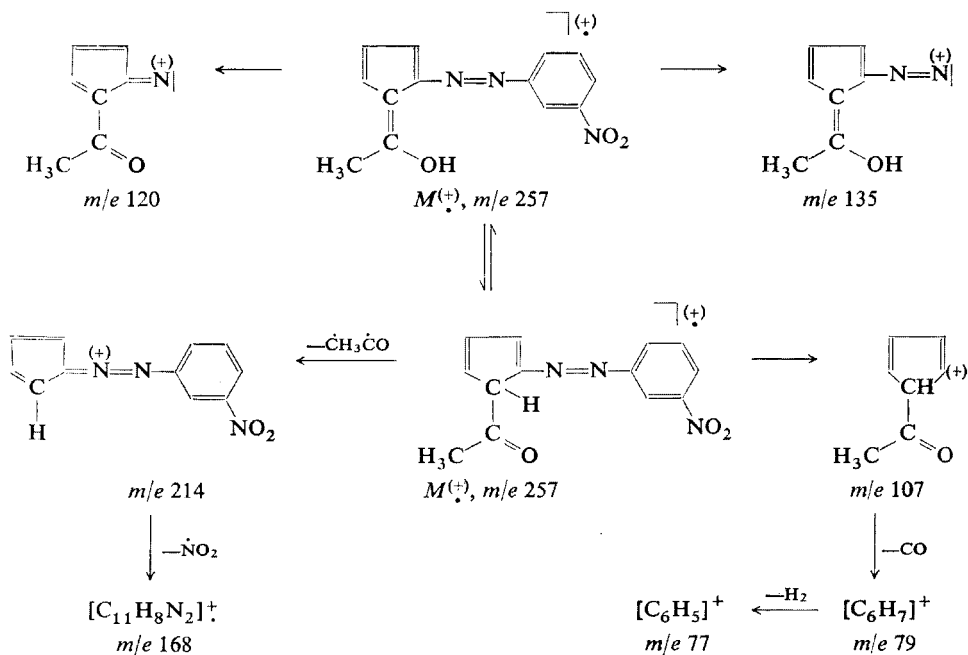


amounts of 2-*p*-nitrophenyl-1-ferrocenecarbaldehyde and 1'-*p*-nitrophenyl-1-ferrocenecarbaldehyde were isolated.

Arylation of 1,1'-diacetylferrocene (on the basis of the work of Rinehart<sup>12,13</sup>, this compound must decompose faster than acetylferrocene) afforded only the product of the reaction of fulvene with the *p*-nitrobenzenediazonium cation; Nesmejanov and coworkers<sup>4</sup> isolated similarly 6-hydroxy-6-methyl-2-(*p*-nitrophenylazo)fulvene only. We have also isolated a small amount of its arylation product.

All experiments were accompanied by formation of a considerable quantity of polymers insoluble in benzene. Since the isolated coupling products or coupling and arylation products of fulvene are relatively stable, it may be assumed that the polymers are formed from the intermediary fulvene or the coupling product with position 3 of fulvene. The polymers were not subjected to detailed examinations.

It may be seen from Scheme 1 that the reaction course is not as unambiguous as assumed by Nesmejanov and coworkers<sup>3-5</sup> or Bozak and Rinehart<sup>6</sup>. It is however obvious that substituted phenylazofulvenes cannot be formed from the coupling product of acetylferrocene as proposed by Bozak and Rinehart but from 6-hydroxy-6-methylfulvene by coupling or arylation as assumed by the Nesmejanov team<sup>5</sup>. The 6-substituted 6-hydroxy-2-arylazofulvene formed in the first step is relatively stable in view of a strong intramolecular hydrogen bond (proved by PMR spectra;



SCHEME 2

$\delta_{\text{OH}} \sim 15$  p.p.m.) and is thus susceptible to further substitution reactions. Such an additional stabilisation is not possible in the case of the isomeric 3-arylazofulvene and for this reason no derivatives of this type have been isolated.

The structure of products was unambiguously established by interpretation of PMR spectra (Table I). The spectra of arylazofulvenes were very similar to those reported by Bozak and Rinehart<sup>6</sup>, *cf.* the presence of methyl groups ( $\delta \sim 8.4$  p.p.m.) or hydrogen attached to C<sub>6</sub> carbon atom of the fulvene ( $\delta \sim 9.4$  p.p.m.), aromatic protons ( $\delta \sim 7.4-8.4$  p.p.m.), a hydroxylic group with a strong hydrogen bond ( $\delta_{\text{OH}} 15$  p.p.m.) and three multiplets of protons attached to C<sub>3</sub>, C<sub>4</sub>, and C<sub>5</sub> carbon atoms of fulvene. In spectral measurements of arylated arylazofulvenes, the integrated record of PMR and mass spectra indicated the presence of benzene in substances previously crystallised from benzene in spite of thorough drying. One recrystallisation from methanol was sufficient to obtain fair PMR spectra. Thanks to the solubility of both isomers obtained by arylation of ferrocenecarbaldehyde with *p*-bromobenzenediazonium sulfate, the PMR spectra were measured and the position of aryls on the arylazofulvene nucleus was unequivocally determined by means of the spectral analysis, particularly on the basis of coupling constants.

The structure of arylation products of acetylferrocene (Table II) was established as follows. The spectrum of 1-acetyl-1'-(*p*-nitrophenyl)ferrocene or 1-acetyl-1'-(*m*-nitrophenyl)ferrocene lack the proton signal of a substituted cyclopentadienyl ring. 1-Acetyl-2-(*p*-nitrophenyl)ferrocene exhibits signals of hydrogens of an unsubstituted cyclopentadienyl ring ( $\delta = 4.25$  p.p.m.) and multiplets of hydrogens 3, 4, and 5 of a disubstituted cyclopentadienyl ring. 1-Acetyl-3-(*p*-nitrophenyl)ferrocene was proved only in the mixture with the 2-isomer (compound X). The spectrum of the mixture exhibits two singlets belonging to the C<sub>5</sub>H<sub>5</sub> residue at  $\delta$  4.25 and 4.12 p.p.m. of the relative intensity 1 : 3 and an extended singlet of methyl groups at  $\delta$  2.47 p.p.m. In the ferrocene region, the spectrum of a mixture of diarylated or tri-

TABLE III  
Composition of Some Ions in Mass Spectrum of Compound IV

63	C <sub>5</sub> H <sub>3</sub>	63-0235,	63-0231
77	C <sub>6</sub> H <sub>5</sub>	77-0391,	77-0393
78	C <sub>5</sub> H <sub>4</sub> N	78-0344,	78-0349
79	C <sub>6</sub> H <sub>7</sub>	79-0548,	79-0537
92	C <sub>6</sub> H <sub>4</sub> O	92-0262,	92-0262
120	C <sub>7</sub> H <sub>6</sub> NO	120-0449,	120-0452
151	C <sub>7</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub>	151-0507,	151-0508
210	C <sub>13</sub> H <sub>10</sub> N <sub>2</sub> O	210-0793,	210-0803

arylated products shows only multiplets of substituted cyclopentadienyl rings. From three different signals of methyl protons (ratio, 1.5 : 1.5 : 1; chemical shifts, 2.7 : 2.5 : 2.13  $\delta$ ) it may be inferred that a three-component mixture of 1-acetyl-1',2-bis(*p*-nitrophenyl)ferrocene, 1-acetyl-1',3-bis(*p*-nitrophenyl)ferrocene, and a triarylated derivative is involved. The presence of the triarylated derivative follows from the integrated record (a greater area belongs to the aromatic protons than it could be expected in the case of diarylated isomers) as well as from elemental analysis. The single pure diarylated isomer isolated was ascribed the structure of 1-acetyl-2,5-bis(*p*-nitrophenyl)ferrocene.

The mass spectra of 6-hydroxy-2-aryloxy-6-substituted fulvenes (compounds *II* and *IV*) and 6-hydroxy-3-aryl-2-aryloxy-6-substituted fulvenes (compounds *I*, *V*, and *XIV*) or 6-hydroxy-6-substituted fulvenes (compounds *VI* and *XVI*) were also taken.

The basic ion in the mass spectrum of 6-hydroxy-2-(*m*-nitrophenylazo)-6-methylfulvene (*IV*) is the molecular ion  $m/e$  257 (Fig. 1). The basic fragmentation paths are shown on Scheme 2. Of interest is the elimination of 43 mass units in the form of the  $\text{CH}_3\text{CO}$  radical (or  $\text{CH}_3 + \text{CO}$ ). This finding indicates the transformation of the molecular ion into the "keto" form as also established by the mass spectrum

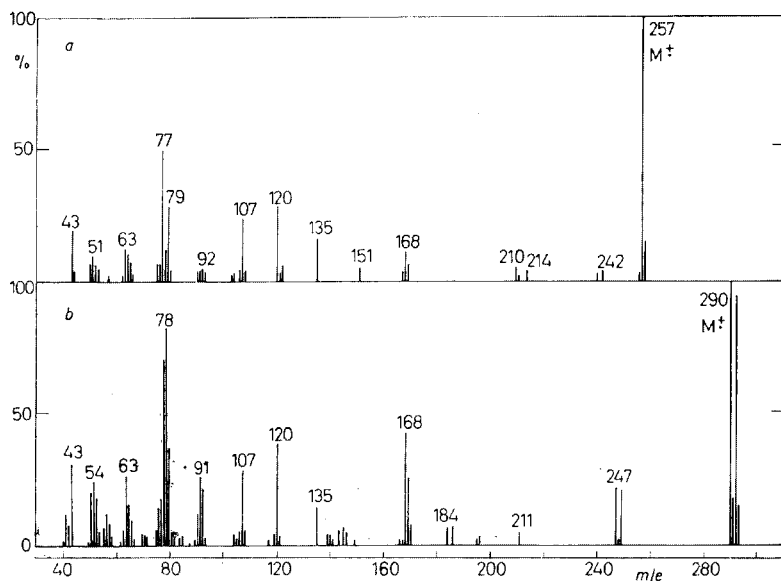


FIG. 1

Mass Spectra of *a* 6-Hydroxy-2-(*m*-nitrophenylazo)-6-methylfulvene (*IV*) and *b* 6-Hydroxy-2-(*p*-bromophenylazo)-6-methylfulvene

of the partly deuterated sample (40% of the 6-OD isomer) since the deuterium was present in fragments containing the cyclopentadiene ring. Other ions in the region of higher masses:  $M - 15$  ( $M - \text{CH}_3$ ),  $M - 17$  ( $M - \text{OH}$ ),  $M - 46$  ( $M - \text{NO}_2$ ), and  $M - 47$  ( $M - \text{HNO}_2$ ). Composition of some ions in the spectrum of compound *IV* was inferred by measurement of exact masses (Table III).

The mass spectrum of compound *II* is shown on Fig. 1. The presence of one bromo atom may be inferred from relative intensities of molecular ions  $m/e$  290 and  $m/e$  292. The basic paths of the fragmentation process except for the elimination of the bromo atom ( $M - 79$ ) are analogous to those of compound *IV*.

In mass spectra of arylated 6-hydroxy-2-aryloxy-6-substituted fulvenes *I*, *V*, *XIV*, *VI*, and *XVI*, the molecular ion  $M^+$  was the most intensive one. The basic cleavage was similar to that of compounds *II* and *IV*. The spectra are not shown because of the insufficient purity of samples. The spectra also suggested traces of the starting material, *i.e.*, substituted anilines, as well as disubstituted diphenyls which may represent the by-products of the reaction. The removal of contaminants by repeated chromatography or crystallisation failed. All substances subjected to PMR measurements were homogeneous on thin-layer chromatography (one spot).

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