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APPLICATION OF INTERNAL MICHAEL ADDITION TO THE SYNTHESIS OF [*n*]FERROCENOPHANE DERIVATIVES

II. SYNTHESIS OF [*n*]FERROCENOPHANE DERIVATIVES CONTAINING ONE OR TWO PHENYLENE GROUPS IN THE BRIDGE

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SUMMARY

The syntheses of ferrocenophane derivatives with one *m*-phenylene group or two *m*- or *p*-phenylene groups between the ferrocene system and the five-membered bridge are described.

INTRODUCTION

The application of internal Michael addition to the synthesis of [5]ferrocenophane[1–3], [4]ferrocenophane[4,5], [3]- and [7]ferrocenophane[5] derivatives has been described previously. We describe attempts to introduce phenylene groups into the bridge system of ferrocenophanes.

RESULTS AND DISCUSSION

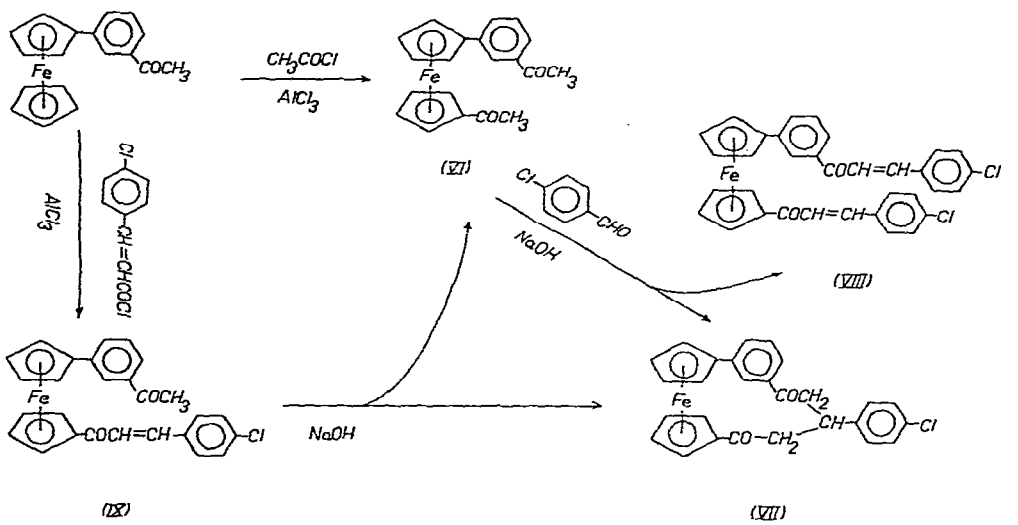
We carried out several experiments using (*p*-acetylphenyl)ferrocene as starting material and intended to lead to 3-(*p*-chlorophenyl)-1,5-dioxo[5]paracyclo[0](1,1')-ferrocenophane*. The product of acetylation of (*p*-acetylphenyl)ferrocene, 1-acetyl-1'-(*p*-acetylphenyl)ferrocene (I) was condensed with *p*-chlorobenzaldehyde. All the possible condensation products *viz* 1-(*p*-chlorocinnamoyl)-1'-[*p*-(*p*-chlorocinnamoyl)phenyl]ferrocene (II), 1-(*p*-acetylphenyl)-1'-(*p*-chlorocinnamoyl)ferrocene (III) and 1-acetyl-1'-[*p*-(*p*-chlorocinnamoyl)phenyl]ferrocene (IV) were observed. Compound (II) was the main product isolated, because of its insolubility in the reaction medium. Product (III) was shown to be identical with the product of acylation of (*p*-acetylphenyl)ferrocene with *p*-chlorocinnamic acid chloride. The structure of (IV) was also established by comparison with an authentic sample synthesised by condensation of (*p*-acetylphenyl)ferrocene with *p*-chlorobenzaldehyde to give [(*p*-chlorocinnamoyl)phenyl]ferrocene, (V), which upon Friedel–Crafts acetylation gave (IV) in fair yield.

* The phane nomenclature in ref. 6 is used throughout this work.

An attempt to cyclize (III) was unsuccessful, a *retro*-Claisen–Schmidt reaction taking place instead. A possible explanation of this might lie in the considerable strain which could be caused by ring tilting in the cyclized product.

The reactions which led to 3-(*p*-chlorophenyl)-1,5-dioxo[5]metacyclo-[0](1,1')ferrocenophane (VII) are illustrated in Scheme 1, and it will be seen that the

SCHEME 1

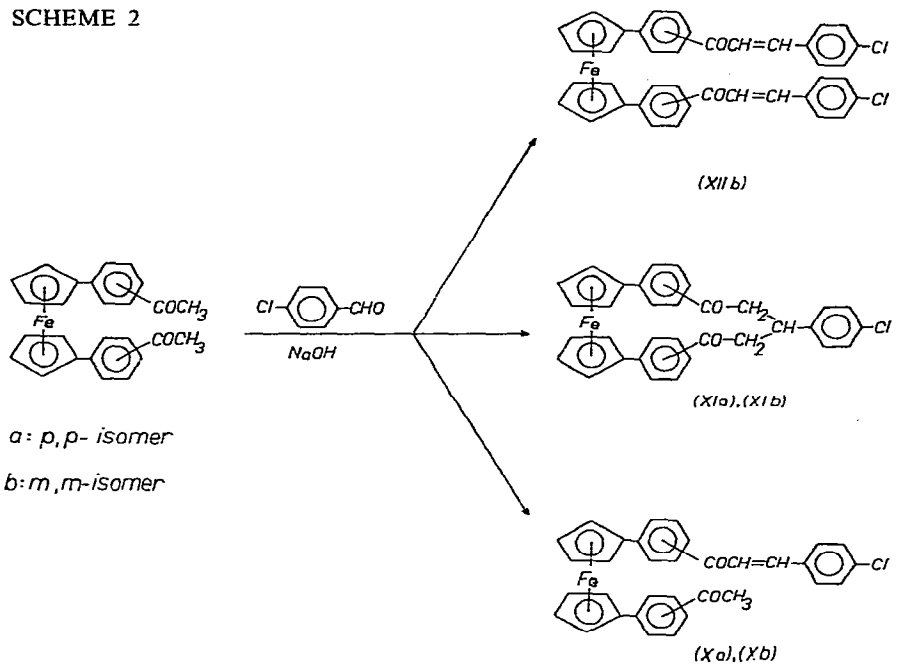


cyclized product (VII) was formed directly by condensation of 1-acetyl-1'-(*m*-acetylphenyl)ferrocene (VI) with *p*-chlorobenzaldehyde as well as by cyclization of 1-(*m*-acetylphenyl)-1'-(*p*-chlorocinnamoyl)ferrocene (IX). The yields were higher in the latter case, but much lower than the yields of [5]ferrocenophane derivatives prepared by a similar route[2,3], possibly because of a strain in the bridge.

Condensation of 1,1'-bis(*m*-acetylphenyl) and 1,1'-bis(*p*-acetylphenyl)ferrocene with *p*-chlorobenzaldehyde in an alkaline medium gave rise to the products shown in Scheme 2.

The cyclisate was obtained among other compounds from 1,1'-bis(*m*-acetylphenyl)ferrocene when the reaction was carried out in ethanol. The condensation involving 1,1'-bis(*p*-acetylphenyl)ferrocene under the same conditions stopped at the mono-chalcone (Xa), since this was insoluble in the reaction medium and precipitated out. An attempt to cyclize this chalcone (Xa) in a larger volume of ethanol was successful. Excellent yields of 3-(*p*-chlorophenyl)-1,5-dioxo[5]paracyclo[0]-(1,1')ferroceno [0]paracyclophane were obtained when the reaction was carried out in DMF; the yields of 3-(*p*-chlorophenyl)-1,5-dioxo[5]metacyclo[0](1,1') ferroceno[0]metacyclophane and 3-(*p*-chlorophenyl)-1,5-dioxo[5]metacyclo[0](1,1') ferrocenophane obtained in this solvent were only moderate, but better than those obtained when ethanol was used.

SCHEME 2



EXPERIMENTAL

All m.p.'s were determined on a Kofler apparatus, and are uncorrected. The IR spectra were measured on a Zeiss UR-20 instrument in the region of 700–3600 cm^{-1}, and the scale was calibrated by use of a polyethylene standard. The physical constants, analyses, and IR spectra of the products are shown in Tables 1 and 2. Yields were calculated with respect to the amount of ferrocene derivative initially used.

Chromatography was carried out on Al_2O_3 (Brockman II-Reanal, Budapest) or SiO_2 (Kavalier, Votice) columns, with benzene containing 3% of ethyl acetate as eluant. The products are listed in the sequence of elution from the column.

The (acetylaryl)ferrocenes were prepared by arylation of ferrocene with the corresponding aryldiazonium sulphate[7]. The physical constants of (*p*-acetylphenyl)-ferrocene, (*m*-acetylphenyl)ferrocene and 1,1'-bis(*p*-acetylphenyl)ferrocene were in agreement with literature data[8–10]. The synthesis of 1,1'-bis(*m*-acetylphenyl)ferrocene (m.p. 145–147°) will be described elsewhere[11].

Preparation of 1-*acetyl*-1'-(*p*-*acetylphenyl*)*ferrocene* (*I*)

The solution of 2.15 ml (0.03 mole) of acetyl chloride and 8 g (0.06 mole) of anhydrous $AlCl_3$ in 100 ml of dichloromethane was slowly added to a stirred solution of 6.1 g (0.02 mole) of (*p*-acetylphenyl)ferrocene in 100 ml of dichloromethane. The reaction mixture was stirred for 4 h at room temperature and then added to water.

After the usual work-up, involving extraction, drying, evaporation of the solvent etc., as described in ref. 12, chromatography on Al_2O_3 yielded 2 g (35%) of the starting material, and orange-red crystals (2.2 g, 35%) of 1-acetyl-1'-(*p*-acetyl-phenyl)ferrocene (I).

TABLE 1

ELEMENTAL ANALYSES AND M.P.'S OF PRODUCTS

Compound	*Formula*	*Analysis found (calcd.) (%)*		*M.p. (°C) (solvent)*	*Yield (%)*
		Fe	*Cl*		
(I)	$C_{20}H_{18}FeO_2$	16.61 (16.91)		140–143 (benzene/petrol)	35.0
(II)	$C_{34}H_{24}Cl_2FeO_2$	9.40 (9.44)	11.47 (11.98)	241–243 (DMF)	25.0
(III)	$C_{27}H_{21}ClFeO_2$	12.06) (11.91)	7.54 (7.56)	158–160 (petrol)	45.0
(IIIa)	$C_{27}H_{21}ClFeO_2$	11.50 (11.91)	7.32 (7.56)	224–226 (benzene/petrol)	10.0
(IV)	$C_{27}H_{21}ClFeO_2$	12.30 (11.91)	7.53 (7.56)	187–188 (benzene)	45.0
(V)	$C_{25}H_{19}ClFeO$	12.44 (13.08)	8.13 (8.30)	223–225 (benzene)	51.0
(VI)	$C_{20}H_{18}FeO_2$	16.65 (16.91)		76–77 (petrol)	90.0
(VII)	$C_{27}H_{21}ClFeO_2$	11.91 (11.91)	7.20 (7.56)	221–224 (benzene/petrol)	11.0
(VIII)	$C_{34}H_{24}Cl_2O_2$	9.72 (9.44)	12.54 (11.98)	169–172 (acetone/petrol)	23.0
(IX)	$C_{27}H_{21}ClFeO_2$	12.10 (11.91)	7.81 (7.56)	99–101 (benzene/petrol)	54.3
(Xa)	$C_{33}H_{25}ClFeO_2$	10.13 (10.02)	6.86 (6.57)	209–210 (benzene)	10.0
(Xb)	$C_{33}H_{25}ClFeO_2$	10.00 (10.02)	6.40 (6.57)	154–157 (benzene/petrol)	14.7
(XIa)	$C_{33}H_{25}ClFeO_2$	9.65 (10.02)	6.06 (6.57)	>360 (DMF)	80.0
(XIb)	$C_{33}H_{25}ClFeO_2$	9.71 (10.02)	5.68 (6.57)	230–235 (benzene/petrol)	25.0
(XIIb)	$C_{40}H_{28}Cl_2FeO_2$	8.20 (8.30)	10.73 (10.60)	215–217 (benzene/petrol)	4.4

Other acylations

The other acylations were carried out analogously.

(*i*). Acylation of 1.5 g of [*p*-(*p*-chlorocinnamoyl)phenyl]ferrocene (IV) with acetyl chloride gave a small amount of the starting material and 0.75 g (45%) of 1-acetyl-1'-[*p*-(*p*-chlorocinnamoyl)phenyl]ferrocene.

(*ii*). Acylation of (*p*-acetylphenyl)ferrocene (4.5 g) with *p*-chlorocinnamic acid chloride gave 0.5 g (17%) of the starting material, 0.7 g (10%) of deep red crystals of 1-(*p*-acetylphenyl)-2-(*p*-chlorocinnamoyl)ferrocene (IIIa), and 3.5 g (45%) of red crystals of 1-(*p*-acetylphenyl)-1'-(*p*-chlorocinnamoyl)ferrocene (III).

(*iii*), Acylation of (*m*-acetylphenyl)ferrocene (6.1 g) with acetyl chloride gave 0.5 g (8.2%) of starting material and 6 g (90%) of 1-acetyl-1'-(*m*-acetylphenyl)ferrocene (VI).

(*iv*). Acylation of (*m*-acetylphenyl)ferrocene (4.6 g) with *p*-chlorocinnamic acid

TABLE 2

CHARACTERISTIC IR FREQUENCIES OF PRODUCTS SYNTHESIZED

All spectra were measured in Nujol; frequencies in cm^{-1}.

Compound	*Cp ring*		ν_s(Cp–$COCH_3$)	γ[C=C (C_6H_5)]	ν(CO)
	1000–1023	1100–1107	1113–1118		
(I)	1023		1113	1570	1608, 1680
(II)	1012			1568, 1595	1665, 1676
(III)	1012		1115	1569, 1605	1659, 1681
(IIIa)	1013	1108	1120	1568, 1595, 1608	1655, 1678
(IV)	1015		1118	1604, 1618	1670
(V)	1012	1108		1600, 1612	1663
(VI)	1018		1115	1605	1659, 1685
(VII)	1015			1583, 1612	1665, 1680
(VIII)	1010	1111		1570, 1595, 1615	1656, 1666
(IX)	1012			1568, 1595	1655, 1683
(Xa)	1017		1118	1573, 1613	1664, 1680
(Xb)	1012		1113	1596, 1613	1670, 1687
(XIa)	1015	1108		1570, 1608	1673
(XIb)	1013	1108		1585, 1603	1678
(XII)	1013			1572, 1600, 1615	1664

chloride gave 0.7 g (15%) of the starting material and 2.5 g (54.3%) of 1-(*m*-acetylphenyl)-1′-(*p*-chlorocinnamoyl)ferrocene (IX).

Interaction of 1-*acetyl*-1′-(*p-acetylphenyl*)*ferrocene with p-chlorobenzaldehyde*

A mixture of 4.95 g (0.015 mole) of 1-acetyl-1′-(*p*-acetylphenyl)ferrocene and 2.1 g (0.015 mole) of *p*-chlorobenzaldehyde in 300 ml of methanol was stirred and heated to 40–50°. Then 25 ml of 10% NaOH was added and the mixture was stirred under reflux for 4 h. The red precipitate was filtered off, washed with water and dried. It was extracted with benzene, the insoluble material being filtered off and crystallized from DMF to give crystals of 1-(*p*-chlorocinnamoyl)-1′-[*p*-(*p*-chlorocinnamoyl)-phenyl]ferrocene (II) (2 g, 25%) were obtained. The benzene solution was chromatographed on SiO_2 to give a small amount of (II), 0.9 g (13%) of 1-(*p*-acetylphenyl)-1′-(*p*-chlorocinnamoyl)ferrocene (III), a small amount of 1-acetyl-1′-[*p*-(*p*-chlorocinnamoyl)phenyl]ferrocene (IV), and 1.3 g (26%) of starting material.

Preparation of [*p*-(*p-chlorocinnamoyl*)*phenyl*]*ferrocene* (*V*)

Condensation of (*p*-acetylphenyl)ferrocene (2.3 g) with *p*-chlorobenzaldehyde was carried out similarly. The solid precipitated after cooling of the reaction mixture, was filtered, washed with water and dried, to give orange crystals (1.7 g, 51%) of [*p*-(*p*-chlorocinnamoyl)phenyl]ferrocene (V).

Interaction of 1-*acetyl*-1′-(*m-acetylphenyl*)*ferrocene with p-chlorobenzaldehyde*

Analogous treatment of 4.95 g of 1-acetyl-1′-(*m*-acetylphenyl)ferrocene with *p*-chlorobenzaldehyde gave after chromatography on Al_2O_3, 0.2 g (2.3%) of 3-(*p*-chlorophenyl)-1,5-dioxo[5]metacyclo[0](1,1′)ferrocenophane (VII) (red crystals),

a small amount of unidentified material, a small amount of the starting material, and violet crystals (2 g, 23 %) of 1-(*p*-chlorocinnamoyl)-1'-[*m*-(*p*-chlorocinnamoyl)phenyl]-ferrocene (VIII).

Attempt to cyclize 1-(p-acetylphenyl)-1'-(p-chlorocinnamoyl)ferrocene

A mixture of 1.9 g (0.004 mole) of 1-(*p*-acetylphenyl)-1'-(*p*-chlorocinnamoyl)-ferrocene and 1.2 g (0.03 mole) of NaOH in 140 ml of ethanol was stirred under reflux for 30 min. It was then added to water and the usual work up, culminating with chromatography on Al_2O_3, gave 0.3 g (23%) of 1-acetyl-1'-(*p*-acetylphenyl)ferrocene (I), 0.3 g (15.7%) of the starting material, and 0.3 g of an unidentified product, the elemental analysis of which indicated that it might be some type of autocondensate of (III).

Cyclization of 1-(m-acetylphenyl)-1'-(p-chlorocinnamoyl)ferrocene

Cyclization of 1-(*m*-acetylphenyl)-1'-(*p*-chlorocinnamoyl)ferrocene (0.95 g) was carried out as described above. Chromatography gave 0.1 g (11%) of 3-(*p*-chlorophenyl)-1,5-dioxo[5]metacyclo[0](1,1')ferrocenophane (VII), 0.15 g (16.5%) of starting material, and 0.1 g (16.5%) of 1-acetyl-1'-(*m*-acetylphenyl)ferrocene (VI).

When the reaction was carried out in DMF, under the conditions described under (*B*), below, the yield of the cyclizate (VII) was raised to 33%.

Interaction of 1,1'-bis(p-acetylphenyl)ferrocene with p-chlorobenzaldehyde

(*A*). The reaction conditions were as described for the condensation of 1-acetyl-1'-(*p*-acetylphenyl)ferrocene with *p*-chlorobenzaldehyde.

A mixture of 1.0 g (0.0025 mole) of 1,1'-bis(*p*-acetylphenyl)ferrocene, 0.35 g of *p*-chlorobenzaldehyde and 5 ml of 10% NaOH in 50 ml of ethanol was taken. Chromatography on SiO_2 gave a small amount of unidentified compound (probably the compound involving condensation on both sides), 0.13 g (10%) of 1-(*p*-acetylphenyl)-1'-[*p*-(*p*-chlorocinnamoyl)phenyl]ferrocene (Xa) (as deep-red crystals), and 0.2 g (20%) of starting material.

(*B*). A stirred mixture of 1.5 g (0.0035 mole) of 1,1'-bis(*p*-acetylphenyl)ferrocene and 0.5 g (0.0035 mole) of *p*-chlorobenzaldehyde in 120 ml of DMF was heated to 40–50°, and 7 ml of 10% NaOH were added. The mixture was stirred at a bath temperature of 80–90° for 4 h. The mixture was cooled, and the orange precipitate filtered off, washed with water, and dried, to give 1.2 g (80%) of product, which, after crystallization from DMF, gave 3-(*p*-chlorophenyl)-1,5-dioxo[5]paracyclo[0](1,1')ferroceno[0]paracyclophane (XIa).

The same material (XIa) was isolated from 1-(*p*-acetylphenyl)-1'-[*p*-(*p*-chlorocinnamoyl)phenyl]ferrocene upon refluxing with NaOH in ethanol.

Interaction of 1,1'-bis(m-acetylphenyl)ferrocene with p-chlorobenzaldehyde

Procedure (*A*) above was used with 1.5 g of 1,1'-bis(*m*-acetylphenyl)ferrocene. Chromatography on SiO_2 gave orange-red crystals of 1,1'-bis[*m*-(*p*-chlorocinnamoyl)phenyl]ferrocene (XIIb) (0.1 g, 4.3%), 3-(*p*-chlorophenyl)-1,5-dioxo[5]metacyclo[0](1,1')ferroceno[0]metacyclophane (XIb) (0.12 g, 6.2%), 1-(*m*-acetylphenyl)-1'-[*m*-(*p*-chlorocinnamoyl)phenyl]ferrocene, (Xb) (0.3 g, 14.7%), and 0.1 g (6.6%) of starting material.

The yield of the cyclisate (XIb) was raised to 25% when procedure (*B*) above was used.

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