127. *Ferrocene Derivatives. Part V.* Ferrocenealdehyde.*

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Ferrocene is much more reactive towards Friedel–Crafts acylation than either benzene or anisole. The first acyl substituent deactivates even the unsubstituted ring. The high reactivity of ferrocene is utilised in its conversion into its mono-aldehyde by the *N*-methylformanilide method. This aldehyde shows the typical properties of an aromatic aldehyde; it undergoes the Cannizzaro reaction, has been converted *via* its oxime into ferrocenyl cyanide, and has also been condensed with malonic acid, with α-picoline methiodide, and, in a mixed benzoin condensation, with benzaldehyde. An alternative preparation of the aldehyde is also described.

In our detailed study of the Friedel–Crafts acetylation of ferrocene we sought at least a semiquantitative comparison of the reactivity of ferrocene with that of benzene or its simple derivatives from competitive experiments. Although this quantitative information was not obtained, the results gave us a better understanding of the reactivity of ferrocene and are therefore briefly reported now.

Woodward and his collaborators[1] were the first to prepare diacetylferrocene by this reaction. They had also established[2] that the monoacetyl derivative, whose preparation was subsequently reported from several other laboratories,[3,4] could be obtained efficiently by using a methylene chloride or chloroform solution of the aluminium chloride–acetyl chloride complex. We found that use of equimolecular proportions of ferrocene and of this reagent yields only traces of the disubstitution product. It follows that, under essentially homogeneous reaction conditions, the first substitution step must be very much faster than the second. We believe that this result can only be understood on the basis

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* Part IV, preceding paper.

[1] Woodward, Rosenblum, and Whiting, *J. Amer. Chem. Soc.*, 1952, **74**, 2125.

[2] Woodward *et al.*, personal communication.

[3] Nesmeyanov, Perevalova, Golovnya, and Nesmeyanova, *Doklady Akad. Nauk S.S.S.R.*, 1954, **97**, 459.

[4] Weinmayr, *J. Amer. Chem. Soc.*, 1955, **77**, 3009.

of a very marked deactivating effect exerted by the first substituent towards substitution in the second (unsubstituted) ring, as well as, of course, in the same ring. That acylation with milder Friedel–Crafts catalysts, *e.g.*, stannic chloride,[3] hydrogen fluoride,[4] phosphoric acid,[4a] and, in the present work (recently confirmed by Hauser [5]), boron trifluoride, stops, apparently completely, at the monosubstitution stage confirms this. Similarly other reactions which require relatively reactive aromatic substrates, *e.g.*, aminomethylation [6, 7, 8] and the formylation reported below, lead to exclusive monosubstitution of ferrocene.

Aluminium chloride-catalysed acylation of ferrocene readily leads to disubstitution [1] and this occurs not only with a sufficient excess of acetyl chloride–aluminium chloride complex, but becomes the main result even when excess of aluminium chloride is employed in a reaction in which ferrocene is present in excess over acetyl chloride. This is probably the result of the heterogeneous nature of the reaction under these conditions. (A complex between acetylated ferrocene and aluminium chloride separates rapidly from the chloroform solution, and if this layer may be assumed to extract most of the unchanged acetyl chloride–aluminium chloride complex from the supernatant solution of ferrocene, the above observation is readily accounted for.)

Competitive experiments with benzene and anisole were attempted by using the preformed 1 : 1 acetyl chloride : aluminium chloride complex. Acetylferrocene was the only ketonic product formed in all such experiments and no acetophenone or methoxyacetophenone was detected, although up to 10 : 1 molar ratios of anisole : ferrocene were employed. Even a competitive experiment with phenol afforded acetylferrocene as the only ketonic product, but no attempt was made in this case to find phenyl acetate. These observations clearly indicate that ferrocene is substantially more reactive than anisole and probably at least comparable with phenol. We sought confirmation of this deduction by attempting to couple ferrocene with diazonium salts under conditions applicable to anisole,[9] and were thus led to discover the remarkably facile arylation of ferrocene described in Part II.[10] Independent confirmation has more recently been provided by the demonstation that ferrocene undergoes a Mannich-type condensation with formaldehyde and dimethylamine.[6, 7]

Another consequence was the realisation that the mild methods used to prepare aldehydes from highly reactive aromatic compounds might be applicable to ferrocene. This was substantiated when we treated ferrocene with a mixture of *N*-formylmethylaniline and phosphorus oxychloride.[11, 12] The same method has been employed independently by Rosenblum.[13] *

We have also obtained ferrocenecarboxyaldehyde (I) from dimethylaminomethylferrocene methiodide [6, 7, 8] by the Sommelet reaction, using the procedure introduced by Hewett.[14] Lindsay and Hauser [7] recently used the same starting material for a two-step preparation of the aldehyde (I). This compound yields the usual carbonyl derivatives, but is not very reactive. For instance, it is not extracted from ethereal solution by saturated aqueous bisulphite, although the solid reacts with this reagent. Ethylene glycol converts the aldehyde (I) into the cyclic acetal (II), but the extreme ease with which

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* After this paper was submitted a further preparation of the aldehyde by this method, but under less favourable experimental conditions, was described by Graham *et al.*,[4a] who also report alternative procedures for its conversion into ferrocenylmethanol and ferrocenyl cyanide.

[4a] Graham, Lindsey, Parshall, Peterson, and Whitman, *J. Amer. Chem. Soc.*, 1957, **79**, 3416.

[5] Hauser and Lindsay, *J. Org. Chem.*, 1957, **22**, 482.

[6] *Idem, ibid.*, 1956, **21**, 382.

[7] Lindsay and Hauser, *ibid.*, 1957, **22**, 355.

[8] Part VI, following paper.

[9] Meyer and Lenhardt, *Annalen*, 1913, **398**, 66; Meyer, Irschick, and Schlösser, *Ber.*, 1914, **47**, 1741.

[10] Part II, *J.*, 1955, 367.

[11] Broadhead, Thesis, Sheffield, July 1956.

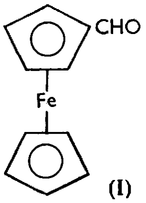
[12] Broadhead, Osgerby, and Pauson, *Chem. and Ind.*, 1957, 209.

[13] Rosenblum, *ibid.*, 1957, 72.

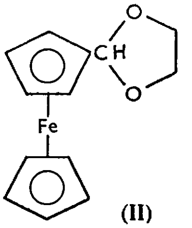
[14] Hewett, *J.*, 1940, 293; cf. Badger, *J.*, 1941, 535; Angyal, Morris, Tetaz, and Wilson, *J.*, 1950, 2141.

this acetal hydrolyses back to the aldehyde (I) precluded the use of this protective device for further substitutions designed to yield, *e.g.*, the dialdehydes.

The oxime of the aldehyde has been isolated in both *syn*- and *anti*-forms and these have both been converted into the corresponding nitrile (III). This dehydration resulted, in place of Beckmann rearrangement, when the oxime was treated with phosphorus pentachloride, and again when an isomerisation to the amide was attempted by the Raney nickel method.[15] Conversion into the nitrile proceeded more smoothly with acetic anhydride, but the most efficient method found for the dehydration of either stereoisomer of the oxime was the use of di*cyclo*hexylcarbodi-imide.† Ferrocenyl cyanide has also been obtained in minute yield by direct Friedel–Crafts reaction of ferrocene with cyanogen bromide.



(I)



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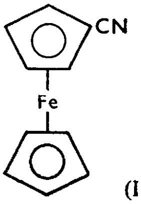

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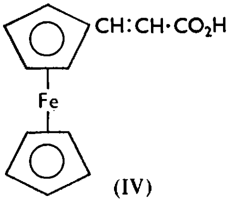

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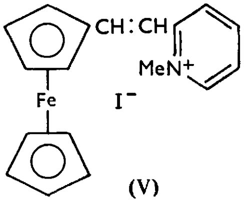

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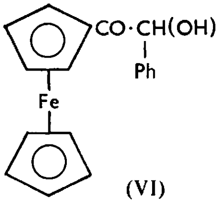

(VI)

The aldehyde (I) is stable to dilute alkalis, and the Cannizzaro reaction proceeded only under rather vigorous conditions. An attempted " crossed Cannizzaro reaction " with formaldehyde did not improve the yield of ferrocenylmethanol. The latter was best obtained by reduction of the aldehyde with sodium borohydride. The aldehyde (I) condenses smoothly with typical compounds containing reactive methylene groups, *e.g.*, with malonic acid yielding ferrocenylacrylic acid (IV), with hippuric acid,[8] and with 1:2-dimethylpyridinium iodide giving the purple stilbazole (V). The aldehyde was, however, recovered unchanged from an attempted benzoin condensation, although, when a mixture with an equimolecular amount of benzaldehyde was treated under the same conditions, the acyloin (VI) was formed in moderate yield. That this product has the structure (VI)

TABLE 1. *Infrared carbonyl stretching frequencies* (*in cm.*$^{-1}$; $CHCl_3$ *solution*).

	R·CHO	R·CO·CH$_3$	R·CO·CH(OH)·C$_6$H$_5$ [a]
R = C_6H_5	1703 [b]	1683 [b]	1681
R = $C_{10}H_9Fe$	1676, 1666 [c]	1672 [d]	1668, 1648

[a] As KBr disc. [b] Hartwell *et al.*[16] give 1705 and 1687 cm.$^{-1}$ for liquid benzaldehyde and acetophenone, respectively. [c] The exact figures are doubtful (within perhaps 5 cm.$^{-1}$) owing to incomplete resolution of this doublet, but the average (1671) should be comparable with the other figures quoted. Failure to recognise this band as a doublet undoubtedly accounts for the discrepancy between the values previously recorded.[12, 13] The values now observed for KBr discs, both of this compound and of acetylferrocene, are within experimental error (±2 cm.$^{-1}$) of those observed in solution. [d] Rosenblum [17] gives 1675 cm.$^{-1}$.

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† The use of this reagent was suggested to us by Dr. D. T. Elmore. It does not appear to have been employed previously for the dehydration of oximes.

[15] Paul, *Bull. Soc. chim. France*, 1937, **4**, 1115.

[16] Hartwell, Richards, and Thompson, *J.*, 1948, 1436.

[17] Rosenblum, Thesis, Harvard, 1953.

rather than the tautomeric benzoyl-ferrocenylmethanol structure follows from a comparison of the carbonyl stretching frequencies listed in Table 1. In common with the other two ferrocene derivatives, the product (VI) absorbs at a lower frequency than the corresponding benzene derivatives. This difference is particularly large in the case of the two aldehydes—a fact which emphasises the strong polarisation of the carbonyl group in ferrocenecarboxyaldehyde. This is also indicated by its basicity—the aldehyde (I) can be extracted from organic solvents with aqueous hydrochloric acid.

EXPERIMENTAL

" Alumina " used for chromatography refers to Spence's " Type H; 100/200's mesh " which had been partially deactivated by exposure to air for 6 hr.

Acetylation of Ferrocene and Acetylferrocene.—The reagent used in all experiments was prepared by dissolving a known weight of acetyl chloride in dry alcohol-free chloroform and allowing this solution to stand in contact with excess of aluminium chloride for 2 hr. Addition of water to such solutions followed by gravimetric estimation of aluminium by the oxine method indicated that 90% of the aluminium chloride required to form a 1 : 1 AcCl : $AlCl_3$ complex had been dissolved. This reagent was added during 15—20 min. to a stirred solution of ferrocene in chloroform, under nitrogen at 0° (Table 2). [Results (not listed) obtained at 20° were similar, but yields decreased with time owing to the formation of tars.] After stirring for the time specified, ice was added to the reaction mixture together with sufficient titanous sulphate solution to reduce any ferricinium salt present. The organic layer was separated, dried, and evaporated, and the residue chromatographed on alumina with benzene as solvent.

TABLE 2.

Ferrocene (moles)	AcCl (moles)	Time [a] (hr.)	Ferrocene recovered (%)	Acetyl-ferrocene [b] (%)	Diacetyl-ferrocene [b] (%)	Total ferrocene accounted for (%)
0·013	0·013	0·5	53	47 [c] (89)	tr.[d]	95
0·011	0·011	0·5	50	47 [c] (86)	tr.[d]	92
0·018	0·018	1·5	44	54 [c] (86)	tr.[d]	92
0·016	0·05	1	0	3 [e]	73 [e]	76
0·018	0·09	1·5	6	15 [e] (17)	71 [e] (76)	92
0·02	0·018 [f]	1·5	56	9·7 [c] (20) 8·8 [e]	54 [c] (56) 24·5 [e]	89
0·016	0·016 [g]	5	55	13 [e] (26)	19 [e] (38)	85

[a] Includes time of addition. [b] Yields in parentheses are corrected for recovered ferrocene. [c] Based on AcCl–$AlCl_3$ complex assuming 90% formation from AcCl. [d] Nil or trace (less than 0·5%). [e] Based on ferrocene. [f] Additional $AlCl_3$ (2·7 g.; 0·02 mole) added to the ferrocene before addition of AcCl–$AlCl_3$ complex. [g] $AlCl_3$ (6 g.) added as in (*f*).

Similar acetylations of acetylferrocene were found to require the addition of solid aluminium chloride and then gave 85% yields of diacetylferrocene and 10% of unchanged monoacetyl derivative after 2 hr. (equimolecular amounts of acetylferrocene and acetyl chloride being used). Without free aluminium chloride only 1% of diacetylferrocene was formed, probably owing to preferential complex formation by the acetylferrocene which therefore abstracted the aluminium chloride from the 1 : 1 acetyl chloride–aluminium chloride complex added to it.

Preparation of Acetylferrocene by Use of Acetic Anhydride–Boron Trifluoride.—Ferrocene (3 g.; 0·016 mole) and acetic anhydride (1·64 g.; 0·015 mole) were dissolved in dry chloroform and cooled to 0°. Dry boron trifluoride was passed in for 2 hr., and the solution then left for a further 4 hr. at 0°. After working up as above, ferrocene (0·36 g.; 13%) was recovered and acetylferrocene (2·36 g.; 73% based on unrecovered ferrocene) was obtained.

Attempted Competitive Acetylations of Ferrocene and Benzene, Anisole, or Phenol.—These were carried out in the same manner as the experiments listed in Table 2. The reactants were employed in the following proportions (moles), and the yields (based on the complex) were as shown:

	Ferrocene	AcCl	Third component	Yield (%)
(*a*)	0·02	0·014	Benzene, 0·02	50
(*b*)	0·018	0·012	Anisole, 0·018	35
(*c*)	0·018	0·016	,, 0·18	47
(*d*)	0·016	0·016	Phenol, 0·016	9

In experiment (*d*) 91% of the ferrocene was recovered unchanged. No other ketonic products were detected in any of these experiments although it had been demonstrated separately that both acetophenone and *p*-methoxyacetophenone are readily separated from acetylferrocene by chromatography and that both are almost quantitatively precipitated by 2 : 4-dinitrophenylhydrazine under the conditions used.

Ferrocenecarboxyaldehyde (I).—(a) N-*Methylformanilide method. N*-Methylformanilide (4·4 g.; 0·032 mole) and phosphorus oxychloride (5 g.; 0·032 mole) were mixed and left at room temperature for 1 hr. Ferrocene (2·99 g.; 0·016 mole) was then added in small portions with vigorous shaking during approx. 30 min., the mixture being kept cool throughout. It was then left in a stoppered flask for 72 hr. After addition of ice-water, the mixture was left for some hours to ensure complete decomposition of the complex. The product was extracted with chloroform, and the solution dried (Na_2SO_4) and evaporated. A benzene solution of the residue was chromatographed on alumina to separate the product from unchanged ferrocene (0·125 g.; 4·2%) and *N*-methylformanilide. The main red band was eluted with benzene, evaporated, and crystallised from 25% aqueous ethanol to yield *ferrocenecarboxyaldehyde* (I) (2·56 g.; 77·6%), m. p. 119—120°, raised by further crystallisation from the same solvent or from light petroleum (b. p. 40—60°) to 121° (Found: C, 61·4; H, 4·9. $C_{11}H_{10}OFe$ requires C, 61·7; H, 4·7%). This aldehyde is volatile in steam and sublimes at 70°/0·01 mm. Ultraviolet max. in methanol: 226, 271, 344, and 461 mμ (log ε 4·23, 3·88, 3·17, and 2·78).

(b) *Sommelet method.* To ferrocenylmethyltrimethylammonium iodide [5] (4·5 g.; 0·012 mole) dissolved in glacial acetic acid (22 ml.), hexamethylenetetramine (5·7 g.; 0·04 mole) was added, and the mixture boiled for 1 min. The solution was poured into water and extracted with benzene. Evaporation under reduced pressure and recrystallisation from aqueous ethanol yielded the above aldehyde (0·92 g.; 37%).

Ferrocenecarboxyaldoxime.—This compound was isolated in two distinct forms, depending on the method of preparation. Recrystallisation of each form appeared to cause partial conversion into the other, and, as mixtures showed intermediate m. p.s it remains doubtful whether either form has been obtained quite pure. The " α "-form is tentatively assigned the *syn*- and the " β "-form the *anti*-configuration by analogy to the benzaldoximes. In each case the *syn*-isomer has the lower m. p., is more acidic, and is formed under basic reaction conditions, whereas the *anti*-isomer is formed in acidic medium. The " α "-form was produced essentially under the conditions described by Lindsay and Hauser [7] and had the same properties. A sample of the same m. p. (90—92°) was obtained in a preparation carried out as described below, under (*a*), for the " β "-isomer, but in which the product was chromatographed on alumina using benzene as solvent to remove a trace of unchanged aldehyde, and, after removal of the latter, eluted with ethanol. This sample was repeatedly recrystallised from ligroin, and a sample which then had m. p. 96—99° was analysed (Found: C, 57·9; H, 5·0; N, 5·9. Calc. for $C_{11}H_{11}ONFe$: C, 57·7; H, 4·8; N, 6·1%). This isomer dissolves readily in 2N-sodium hydroxide. To recover the oxime from such solutions it is necessary to acidify them carefully at low temperature or, preferably, with solid carbon dioxide, to avoid partial hydrolysis to the free aldehyde.

The " β "-isomer has been obtained by the following two procedures: (*a*) To hydroxylamine hydrochloride (0·7 g.) and anhydrous sodium acetate (1 g.) dissolved in water (4 ml.) were added ferrocenecarboxyaldehyde (I) (1 g.) and enough ethanol (*ca.* 6 ml.) to produce a homogeneous solution on warming. The mixture was refluxed for 2—3 hr., cooled, and extracted with ether, and the ether solution washed repeatedly with 2N-sodium hydroxide. The aqueous layer on acidification yielded only a small amount (less than 0·1 g.) of oxime of very indefinite m. p. The ether layer was dried and evaporated, and the residue crystallised once from benzene, yielding " β "-*ferrocenecarboxyaldoxime* (0·5 g.) as orange prisms, m. p. 155—157°. Four more crystallisations from benzene gradually lowered this m. p. to 145—146° (Found: C, 57·7; H, 4·7; N, 6·25%).

(*b*) A solution of the aldehyde (I) (1·5 g.) and hydroxylamine hydrochloride (0·7 g.) in ethanol (10 ml.) was refluxed under nitrogen for 2 hr. After cooling the black oxime hydrochloride (1·34 g.; 70%) was filtered off. This was suspended in ether, and the free oxime liberated by shaking with sodium carbonate solution. Evaporation of the dried ether solution and crystallisation from benzene afforded the β-oxime, m. p. 150—152°. The product, m. p. 138—140°, described by Rosenblum [13] is presumably predominantly this β-form of the oxime. Graham *et al.*[4a] give m. p. 133—135° for this oxime.

Ferrocenyl Cyanide (III).—(a) *Carbodi-imide method.* The β-oxime (0·15 g.) and di*cyclo*hexylcarbodi-imide (0·17 g.) were refluxed in benzene (10 ml.) for 6 hr. On cooling, di*cyclo*hexylurea (0·12 g.) was filtered off. The benzene solution was then thoroughly extracted with dilute sodium hydroxide, which removed unchanged oxime (15 mg.; 10%). Evaporation of the benzene and crystallisation of the residue from light petroleum afforded the nitrile (97 mg.; 78% based on unrecovered oxime), identical in m. p. and mixed m. p. with the product described under (b). Under identical conditions the α-oxime yielded 70 mg. (50%) of nitrile and 14 mg. (9%) of unchanged oxime.

(b) *Acetic anhydride method.* The oxime (mixed α- and β-) (1 g.) and acetic anhydride (10 ml.) were gently warmed together for 20 min. and then refluxed for a further 20 min. The solution was poured into water (30 ml.) and extracted with chloroform, and the extract washed until neutral, dried, and evaporated. The residue was purified by chromatography on alumina followed by crystallisation from light petroleum (b. p. 40—60°), *ferrocenyl cyanide* (III) forming golden-yellow plates, m. p. 107—108° (Found: C, 62·7; H, 4·5. $C_{11}H_9NFe$ requires C, 62·6; H, 4·3%). Infrared max. in the carbon–nitrogen triple-bond stretching region at 2242 $cm.^{-1}$ (KBr disc).

(c) *Phosphorus pentachloride method.* The oxime (mixed isomers) (1 g.), dissolved in anhydrous ether (25 ml.), was treated with phosphorus pentachloride (1·5 g.). After the initially vigorous reaction had subsided, the mixture was shaken for 2 hr. Chloroform was then added, and ferrocenyl cyanide (0·2 g.; 25%) isolated as above, its identity being established by mixed m. p. and comparison of infrared spectra with the product described under (b).

(d) *By use of Raney nickel.* To the oxime (mixed isomers) (1·8 g.) dissolved in absolute alcohol (40 ml.), a suspension of Raney nickel (approx. 2 g.) in the same solvent was added, and the whole shaken for 48 hr. After addition of water and working up as above, the nitrile (0·1 g.; 6%) was obtained together with unchanged oxime (0·6 g.; 30%) and a trace of free aldehyde (0·04 g.).

(e) *From ferrocene and cyanogen bromide.* To a mixture of ferrocene (6 g.; 0·032 mole), anhydrous aluminium chloride (8·4 g.; 0·06 mole), and carbon disulphide, under nitrogen, a solution of cyanogen bromide (4·24 g.; 0·04 mole) in the same solvent was slowly added at 0°. The mixture was left for 4 hr. and then refluxed for 1 hr. After addition of ice and titanous sulphate solution, the products were worked up as above, yielding unchanged ferrocene (4 g.; 66%) followed on the chromatogram by a trace of ferrocenyl cyanide, identified by its infrared spectrum. All attempts to improve the yield, *e.g.*, by change of solvent, failed.

2-*Ferrocenyl*-1 : 3-*dioxolan* (II).—The aldehyde (I) (2 g.; 0·009 mole) was added to a mixture of benzene, ethylene glycol (1 ml.; 0·018 mole), and a trace of toluene-*p*-sulphonic acid. This mixture was allowed to reflux overnight through a Soxhlet apparatus filled with anhydrous calcium sulphate. Evaporation of the solution and chromatography of the residue on alumina, using *cyclo*hexane as solvent, separated the *cyclic acetal* (II) (2 g.; 94%) from a trace of unchanged aldehyde (0·12 g.; 6%). The acetal crystallised from light petroleum (b. p. 40—60°) as golden-yellow needles, m. p. 81—82° (Found: C, 60·5; H, 5·8. $C_{13}H_{14}O_2Fe$ requires C, 60·5; H, 5·5%).

Ferrocenylmethanol.—(a) *By borohydride reduction.* Addition of sodium borohydride (0·061 g.) to a solution of ferrocenecarboxyaldehyde (I) (0·26 g.) in methanol (5 ml.) caused immediate reduction as indicated by the change in colour from red to yellow. Evaporation of the solvent and recrystallisation from water afforded *ferrocenylmethanol* (hydroxymethylferrocene) (0·216 g.; 85%), m. p. 76° (Found: C, 61·4; H, 5·4. $C_{11}H_{12}OFe$ requires C, 61·2; H, 5·6%).

(b) *By Cannizzaro reaction.* The aldehyde (I) (0·5 g.) was refluxed for 3 hr. with 50% alcoholic potassium hydroxide (10 ml.). After cooling, the mixture was diluted with water and extracted with ether. Evaporation of the ether layer afforded ferrocenylmethanol (0·12 g.; 47%), m. p. (and mixed m. p.) 76°. Acidification of the alkaline layer, extraction with ether, and evaporation of the extract yielded ferrocenecarboxylic acid (0·025 g.; 10%), m. p. 210° (decomp.) undepressed by an authentic specimen.

(c) *By attempted crossed Cannizzaro reaction.* A mixture of ferrocenecarboxyaldehyde (I) (1 g.) and aqueous formaldehyde (1 ml. of 40%) dissolved in methanol (10 ml.) was heated to 65° and treated with potassium hydroxide (2·66 g. dissolved in 2 ml. of water). After refluxing for 3 hr. and working up as above, the neutral product was chromatographed on alumina with benzene as solvent. In this way ferrocenylmethanol (0·045 g.; 9%) was separated from unchanged aldehyde (0·5 g.).

β-*Ferrocenylacrylic Acid* (IV).—The aldehyde (I) (0·5 g.), malonic acid (0·5 g.), and piperidine (10 drops; *ca.* 0·1 ml.) were dissolved in pyridine (12 ml.) and heated under nitrogen on a boiling-water bath for 2 hr. The cooled solution was diluted with water and extracted with chloroform. The chloroform extract was washed with dilute hydrochloric acid and water, and then extracted with 2N-sodium hydroxide. Acidification of the aqueous layer precipitated the brick-red β-*ferrocenylacrylic acid* (IV) (0·4 g.; 68%). Recrystallisation from benzene afforded deep red prisms, m. p. 186—187° (decomp.; efferv.) (Found: C, 61·5, 61·6, 61·7; H, 5·1, 5·2, 5·0; O, 12·4, 12·4. $C_{13}H_{12}O_2Fe$ requires C, 61·0; H, 4·7; O, 12·5%).

1-*Ferrocenyl*-2-(2-*pyridyl*)*ethylene Methiodide* (V).—The aldehyde (I) (0·3 g.), 1 : 2-dimethylpyridinium iodide (0·3 g.) and piperidine (1 ml.) were dissolved in methanol (20 ml.) and refluxed for 3 hr. under nitrogen. On evaporation of the resultant solution to small bulk, the *stilbazole* (V) partly crystallised as deep purple prisms (Found: C, 49·7; H, 4·5; N, 2·9. $C_{18}H_{18}NIFe$ requires C, 50·2; H, 4·2; N, 3·25%). This compound is soluble in polar organic solvents and in water and insoluble in ether or hydrocarbon solvents, but no satisfactory method of recrystallisation has been found.

Mandeloylferrocene (VI).—A mixture of the aldehyde (I) (1·07 g.; 0·005 mole), benzaldehyde (0·53 g.; 0·005 mole), ethanol (15 ml.), and aqueous potassium cyanide (0·5 g. in 1 ml. water) was refluxed for 1·5 hr. After dilution with water and refrigeration for 2 hr. the product was filtered off and recrystallised from aqueous alcohol. The *acyloin* (VI) formed fine pink needles (0·37 g.; 25%), m. p. 148—149° (Found: C, 67·5; H, 5·1. $C_{18}H_{16}O_2Fe$ requires C, 67·5; H, 5·0%).

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