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FORMATION OF 1,2-OLIGOMERIC FERROCENES FROM ULLMANN REACTIONS OF IODOFERROCENES

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Summary

A mixed Ullman reaction between iodoferrocene and 1,2-diiodoferrocene as well as an Ullmann reaction involving only 1,2-diiodoferrocene both produce biferrocene as well as linear 1,2-oligomeric ferrocenes, including 1,2-terferrocene, *meso*-1,2-quaterferrocene, *dl*-1,2-quaterferrocene and several isomeric 1,2-quinqueferrocenes. The formation, spectral characteristics and structures of these products are discussed.

Introduction

Neuse [1] has reported obtaining, among other products, the three isomeric terferrocenes I—III by random combination of ferrocenyl radicals initiated with t-butyl peroxide. 1,1'-Terferrocene (I, m.p. 226—228°C) prepared in this manner was shown to be identical to that prepared by Watanabe, Motoyama, and Hata [2] and also by Roling and Rausch [3]. By an independent and unequivocal synthesis [4], 1,3-terferrocene (II, m.p. 198—200°C) [4] was likewise identified. The remaining terferrocene, also of m.p. 198—200°C, has been assigned [1] as 1,2-terferrocene (III). Goldberg and Breland [5] have described a reputedly unequivocal synthesis of 1,2-terferrocene (III, m.p. 191—193°C) starting from ferrocil * and proceeding via diferrocenylcyclopentadiene, but it appears that their 1,2-terferrocene (III) was impure, possibly being contaminated with the 1,3-isomer (II) [1]. In this paper, we describe Ullmann reactions involving 1,2-diiodoferrocene (V) [6] of known orientation either alone or mixed with iodoferrocene (IV) to produce a variety of 1,2-oligomeric ferrocenes.

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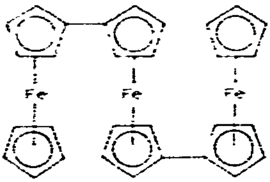
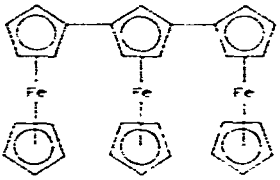
* Ferrocil = diferrocenylglyoxal, FcC(O)C(O)Fc.


(I)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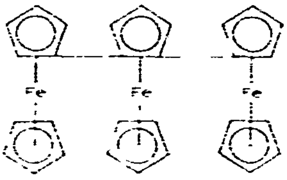
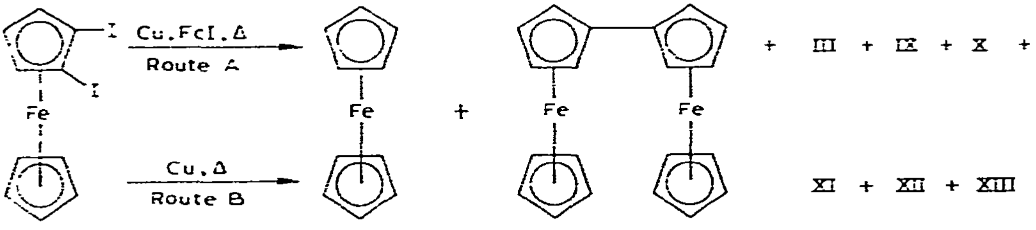

(III)

Results and discussion

In general, the 1,2-oligomeric ferrocenes are more soluble than the 1,1'-oligomeric ferrocenes [3], and as a result are more easily chromatographed with less decomposition on an alumina column. Each oligomer was purified until TLC showed no impurities.

The mixed Ullmann reaction (Scheme 1, Route A) between iodoferrocene (IV) and 1,2-diiodoferrocene (V), and the Ullmann reaction (Scheme 1, Route B) of V alone both produced the same products, although in varying amounts. The yields of products were low for both reactions, and an appreciable amount of dark tarry material was observed that would not chromatograph.

SCHEME 1

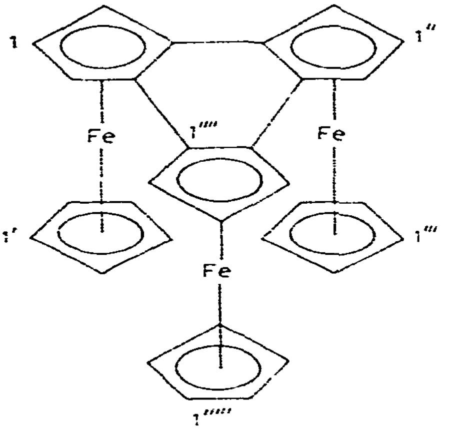


(VI)

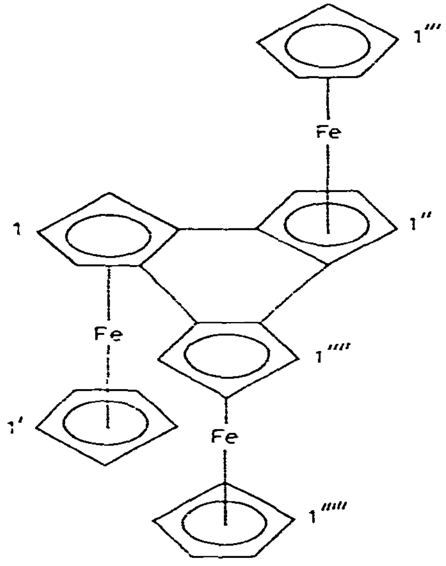
The mixed Ullmann reaction produced biferrocene (VI) by the self-coupling of IV. If the lower yield of VI (average 32%) from this reaction is any indication of the reactivity of the competing 1,2-diiodoferrocene (V), then V is more reactive than is 1,1'-diiodoferrocene, since a 50% yield of VI was obtained under identical conditions in the mixed Ullmann reaction between IV and 1,1'-diiodoferrocene [3].

1,2-Terferrocene (III) produced in both Ullmann reactions should be only the linear compound, as opposed to the possible cyclic products. The two possible 1,2-triferrocenylenes (VII and VIII) would have serious steric interactions for the 1'-, 1'''- and 1'''''-cyclopentadienyl rings in the *cis,cis,cis* isomer (VII) and also steric interactions for the 1'- and 1'''''-cyclopentadienyl rings in the *cis,trans,trans* isomer (VIII).

In addition, cyclic compounds VII and VIII should show high melting points and very low solubility by analogy with the known 1,1'-biferrocenylene [7]. The latter has a fixed configuration and therefore has a very high melting point as well as a very low solubility in comparison to biferrocene (VI) and 1,1'-terferrocene. In contrast, the present 1,2-terferrocene (III, m.p. 202–204°C) is



(VII)

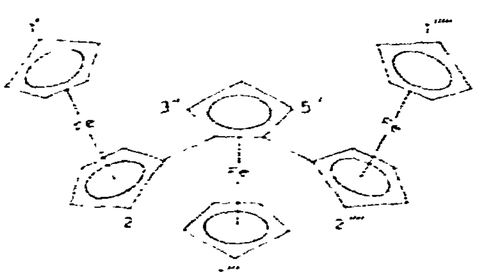


(VIII)

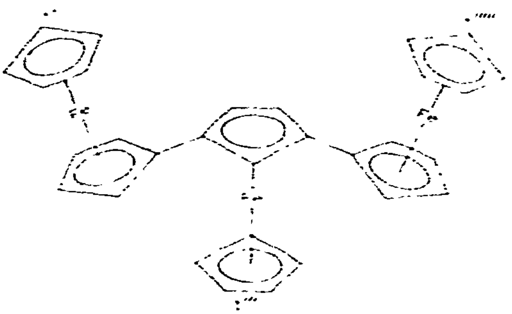
lower melting than VI, 1,1'-terferrocene or 1,1'-biferrocenylene, and the solubility is greater than for any of these compounds. Similarly, the melting point is very close to that of the reported 1,2-terferrocene (III) m.p. 198—200°C) [1] and 1,3-terferrocene (II, m.p. 198—200°C) [4], and a mixed melting point determination of our 1,2-terferrocene with authentic 1,3-terferrocene causes a distinct depression. In analogy with the melting points of isomeric terferrocenes, the melting points of 1,2- and 1,3-diphenylferrocenes are 110 and 107°C, respectively, while 1,1'-diphenylferrocene melts some 40° higher at 155°C [8].

1,2-Terferrocene (III) exhibited polymorphic properties and crystallized from Skellysolve B in four crystalline forms. The melting points were all within a few degrees of one another except one which melted at 187—189°C. Elemental analysis of this low melting terferrocene as well as an elemental analysis of a mixture of the other three polymorphs were in accord with the proposed structure. The IR spectra were all the same, showing bands at 993 and 1100 cm^{-1} for the unsubstituted cyclopentadienyl rings.

The NMR spectrum of III in benzene exhibits two singlets, a multiplet under the singlets, and a multiplet downfield. The downfield singlet (δ 4.13 ppm) is assigned to the $1'''$-protons, since the singlet and the underlying multiplet integrate for ca. nine protons. The upfield singlet at δ 4.04 ppm is then assigned to the $1'$- and $1'''''$-protons of the terminal ferrocenyl units, since integration gives ca. thirteen protons for this peak and the underlying multiplet. The NMR spectrum of 1,3-terferrocene (II) shows the reverse situation, the 10-proton singlet being found at δ 4.02 ppm and the 5-proton singlet at δ 3.82 ppm [4]. The multiplet at δ 4.36 ppm for III integrated for four protons and is assigned to the 2-, $3''$-, $5''$- and $2''''$-protons. These four protons are deshielded since according to molecular models, they lie in the region of the iron atom. Rosenblum [9] has shown that protons held configurationally in the region of the iron atom are



(VII)



(VIII)

deshielded. The rest of the protons in the NMR spectrum of III appear as a multiplet beneath the two singlets.

The UV spectrum of III has absorptions at the same wavelengths as 1,1′-terferrocene [2], and also shows about the same extinction coefficients.

The mass spectrum of III (Table 1) shows a parent ion peak at *m/e* 554 and a doubly charged peak at *m/e* 277. The observed isotopic abundance distribution as seen in Table 2 agrees with the calculated distribution, however, peaks at *m/e* 550, 551, 552 and 553 suggest that the parent molecule can lose two hydrogens to form the 1,2-triferrocenylenes (VII and VIII). The remainder of the fragmentation pattern is similar to that of 1,1′-terferrocene [3].

Upon fractional crystallization of the chromatography band containing 1,2-quaterferrocenes, two crystalline products were obtained, identical under TLC conditions, but with melting points of 250—253°C and 374—376°C. Examination of the combination possibilities from the mixed Ullmann reaction gives rise to two stereoisomers; a *meso* isomer and a pair of enantiomers. The compound of melting point 250—253°C is tenatively assigned as *dl*-1,2-quaterferrocene (IX) for the following reasons. If one examines molecular models of IX it is seen that there is very little room for rotation about the 2″—1‴-bond without encounter-

TABLE 1

MASS SPECTRAL RESULTS FOR 1,2-OLIGOMERIC FERROCENES

m/e	Relative abundance				
	III	IX	X	XI	XII and XIII
922				79	64
738		100	100	100	44
554	100	2	6	8	6
552	23	18	28	25	12
487	3	7	14	71	32
461				26	16
369	2	9	17	26	14
310	4	2	4		
277	11	1			
186	4	4	15	29	100
121	5				
56	3	4	28	[a]	[a]

[a] Peak was off-scale and a value could not be determined.

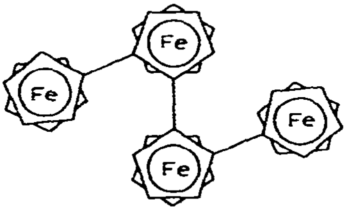
TABLE 2

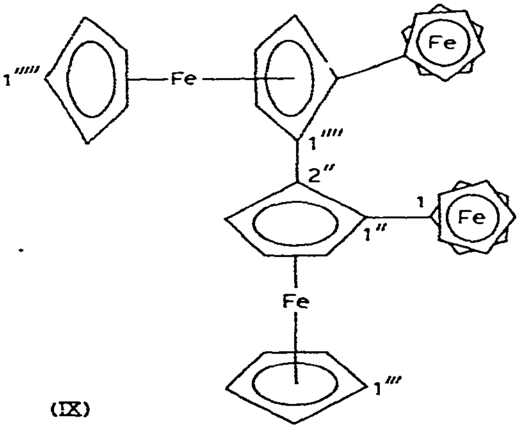
ISOTOPIC ABUNDANCES FOR 1,2-OLIGOMERIC FERROCENES[a]

Mass	III Found (Calcd.)	IX Found (Calcd.)	X Found (Calcd.)	XI Found (Calcd.)	XII and XIII Found (Calcd.)
M + 4	0 (0.2)	0 (0.5)	0 (0.5)	3 (1.1)	1 (1.1)
M + 3	2 (1.4)	3 (3.1)	3 (3.1)	6 (5.8)	6 (5.8)
M + 2	9 (9.0)	16 (15.4)	15 (15.4)	23 (23.2)	19 (23.2)
M + 1	39 (40.4)	52 (53.2)	52 (53.2)	66 (65.1)	56 (65.1)
M	100 (100.0)	100 (100.0)	100 (100.0)	100 (100.0)	100 (100.0)
M − 1	9 (7.2)	13 (12.8)	15 ((12.8)	23 (19.6)	44 (19.6)
M − 2	23 (18.8)	27 (24.8)	27 (24.8)	33 (30.4)	69 (30.4)
M − 3	1 (0.4)	1 (1.2)	1 (1.2)	3 (2.4)	12 (2.4)
M − 4	3 (1.2)	2 (2.3)	3 (2.3)	6 (3.8)	19 (3.8)

[a] Found values are taken from only one spectrum of each product.

ing serious steric hindrance. However, the terminal ferrocenyl groups are able to rotate from the staggered form illustrated to a form in which the ferrocenyl rings are *trans*-disposed about the 1—1″-bond. This type of rotation then suggests that in the NMR spectrum the singlet for the unsubstituted cyclopentadienyl rings of the terminal ferrocenyl units should be in about the same position as the singlet for the terminal ferrocenyl units in 1,2-terferrocene. There is in fact a singlet at δ 4.07 ppm in the NMR spectrum of IX (δ 4.04 ppm for 1,2-terferrocene). The other singlet for the unsubstituted cyclopentadienyl rings of the inner ferrocene units should be slightly more deshielded than the 1‴-protons in 1,2-terferrocene, since the restricted rotation about the 2″—1⁗-bond causes the 1″-

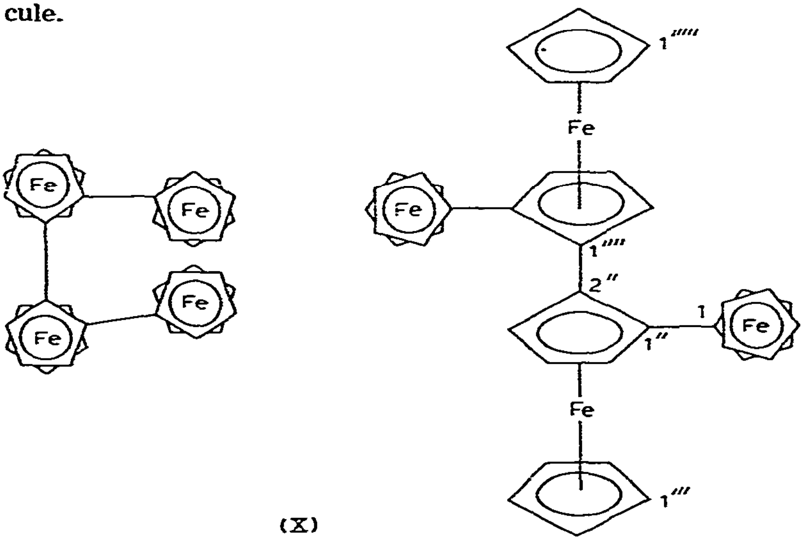




(IX)

cyclopentadienyl ring to deshield the 1'''''-protons, and the 1''''-cyclopentadienyl ring deshields the 1'''-protons. The singlet resonance for these protons appears at δ 4.22 ppm. Due to the relative mobility of the terminal ferrocenyl units of the *dl*-1,2-quaterferrocene (IX) compared to the rigidity of the *meso*-1,2-quaterferrocene (X), the *dl*-isomer should be the more soluble of the two compounds, and this is the case.

Examination of models of *meso*-1,2-quaterferrocene (X) shows that there is very limited rotation about any of the bonds connecting the ferrocene units. Again, the conformation for X as illustrated then indicates that the unsubstituted cyclopentadienyl rings on the inner disubstituted ferrocene units should resemble those of biferrocene. A singlet is indeed observed at δ 4.00 ppm, as is found in biferrocene [10]. The two terminal ferrocenyl units which are held in the staggered conformation should be deshielded by the inner disubstituted cyclopentadienyl rings, and the singlet resonance appears at δ 4.28 ppm. The low solubility of X is also in agreement with the lack of rotation within the molecule.



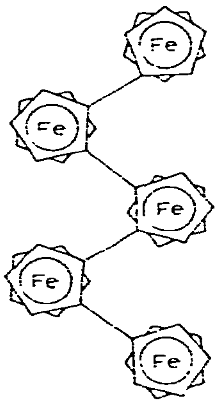
(X)

The IR spectra of the two 1,2-quaterferrocenes (IX and X) are virtually the same, showing peaks at 993 and 1102 cm^{-1} for the unsubstituted cyclopentadienyl rings.

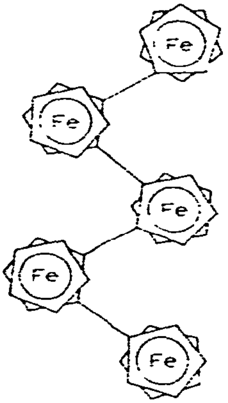
The mass spectra (Table 1) of the 1,2-quaterferrocenes (IX and X) are identical with respect to the number of peaks, but the intensities vary between the two spectra. Both spectra show parent ion peaks at *m/e* 738 and doubly charged ions at *m/e* 369. The observed abundances for the parent ions (Table 2) agree with the calculated abundances, indicating the formation of cyclic compounds such as 1,2-tetraferrocenylenes does not occur in the mass spectrometer.

In the case of the 1,2-quinqueferrocenes, only one apparently pure compound of melting point 345—347°C was isolated. This compound is tentatively assigned as *meso*-1,2-quinqueferrocene (XI), since like the *meso*-1,2-quaterferrocene (X), the solubility of the product is very low. Another product was also isolated which had a wide melting range indicative of a mixture of compounds.

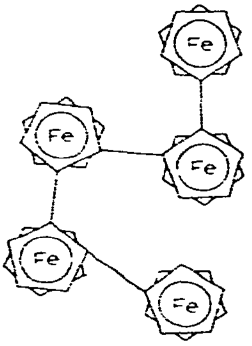
Since random combination in the Ullmann reaction can yield two *meso*-isomers (XI and XII) and a pair of enantiomers (XIII), the mixture possibly contains both XII and XIII.



(XI)



(XII)



(XIII)

The mass spectrum of XI shows the expected parent ion peak at *m/e* 922 and the doubly charged peak at *m/e* 461. The rest of the fragmentation pattern follows that of the 1,2-quaterferrocenes. The observed isotopic abundances agree with the calculated abundances, indicating that no cyclic derivative of the 1,2-quinqueferrocenes was formed in the mass spectrometer and that no cyclic compound was present in the sample. The mass spectrum of the apparent mixture of 1,2-quinqueferrocenes (XII and XIII) also shows the parent ion at *m/e* 922 and the doubly charged ion peak at *m/e* 461. Again, the remainder of the fragmentation pattern resembles that of the 1,2-quaterferrocenes. The isotopic abundances of the peaks representing the molecular ion indicates that another product is present. The peak at *m/e* 920 can be due either to one or more of the 1,2-quinqueferrocenes losing two hydrogens in the mass spectrometer to form a pentaferrocenylene, or to the presence of a pentaferrocenylene in the product formed in the Ullmann reaction.

The IR spectra of the two 1,2-quinqueferrocenes also show bands at 995 and 1102 cm^{-1} for the unsubstituted cyclopentadienyl rings.

From each of the Ullmann reactions there was also obtained material which by TLC could correspond to 1,2-sexiferrocenes, 1,2-septiferrocenes, and 1,2-octaferrocenes. The material in each of these bands separated on the alumina column amounted to only a few mg of product, and because of the large number of stereoisomers possible, purification was not attempted.

It should be noted at this point that the mass spectra of the 1,2-oligomeric ferrocenes show much higher relative abundances for their parent ion peaks than do the 1,1'-oligomeric ferrocenes [3]. Also, there is less of a fragmentation pattern for the 1,2- as compared to the 1,1'-oligomeric ferrocenes [3].

A curious fact is that in Ullmann reactions involving 1,2-diiodoferrocene alone (Scheme 1, Route B), there was isolated in both experiments a considerable amount of ferrocene. The ferrocene that was isolated could only have arisen from breakdown of some of the starting material during the reaction, since there was no possibility of ferrocene being present in the starting material V. Likewise, all the products were linear compounds as opposed to cyclic analogs, indicating hydrogenation of the terminal carbon—halogen bonds. The low yields and the large amount of tarry material that did not chromatograph attest to this hydrogenation and subsequent breakdown of compounds during reaction.

Experimental

NMR spectra were recorded on a Varian A-60 spectrometer, while IR spectra were recorded on a Beckman IR-10 spectrometer. The UV spectrum was recorded on a Cary Model 14 spectrometer. The copper powder used is "Kupfer, KU300, Pulver mind. 99.75%"; it was obtained from the Schuchardt Co., Munich, Germany. The alumina of Activity 3 used in this work was prepared by shaking 1000 g of neutral, activated CAMAG alumina (distributed by Ventron Co., Alfa Division) with 60 ml of water. All columns were packed dry. The dimensions of the column were not considered important as long as the stated amount of alumina was used and the column was packed evenly. Microanalyses were carried out by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts. Skellysolve B is the faction of hydrocarbons boiling between 40—60°C. Melting points are uncorrected and were taken on a Mel-Temp apparatus. Mass spectra were obtained on an AEI MS-9 operating at 70 eV.

1,2-Oligomeric ferrocenes

A typical example is given: In a 50 ml Flask were melted 4.40 g (10 mmol) of 1,2-diiodoferrocene (V) [6] and 1.54 g (4.9 mmol) of iodoferrocene (IV). There was then added 15.9 g (250 mmol) of activated [11] copper powder, a glass stopper was inserted, and the contents of the flask was vigorously shaken. The flask was flushed with nitrogen, restoppered, and placed in an oil bath at 95°C. The temperature was raised throughout the next hour to 150°C and held at this temperature for 23 h. At the end of the heating period, the flask was cooled and the contents extracted repeatedly with 50-ml portions of hot benzene until the extracts were colorless. The benzene solution was cooled and filtered through a column of 75 g of alumina. The filtrate was concentrated to 30 ml and 70 ml of Skellysolve B was added. This solution was placed on a column of 450 g of alumina. The first band was eluted with Skellysolve B to yield 0.13 g of ferrocene.

The second band eluted with a 9/1 mixture of Skellysolve B/benzene gave 0.30 g (33%) of biferrocene (VI), m.p. 238—240°C/dec. (N_2)) (lit. [11] m.p. 238—239°C).

Band three was eluted with a 7/3 mixture of Skellysolve B/benzene to give, after crystallization from Skellysolve B, 0.26 g (17%) of 1,2-terferrocene (III, m.p. 202—204°C (N_2)) (lit. [1] m.p. 198—200°C), mixed m.p. with authentic [4] II, 165—192°C; NMR ($CDCl_3$) singlets at δ 4.10 and 4.13 ppm with a multiplet underneath (22H), multiplet at 4.42 (4H, 2-, $3''$-, $5''$- and $2''''$-protons); NMR (C_6H_6) singlet at δ 4.04 with underlying multiplet (13H, $1'$- and $1''''$-protons plus three other protons), singlet at 4.13 with underlying multiplet (9H, $1'''$-protons and four other protons), multiplet at δ 4.36 (4H, 2-, $3''$-, $5''$- and $2''''$-protons): IR (KBr) 1100 and 995 cm^{-1} (unsubstituted cyclopentadienyl rings); UV (Skellysolve B) λ_{max} 215 (ϵ 209 000), 298 (45 000), 455 (680); mass spectrum *m/e* 554, calcd. mol. wt. 554. (Found: C, 65.24; H, 4.69; Fe, 30.10. $C_{30}H_{26}Fe_3$ calcd.: C, 65.03; H, 4.74; Fe, 30.24%).

The above melting point and elemental analysis applies to a mixture of three of the polymorphs isolated. The fourth polymorph had a m.p. 187—189°C (N_2). (Found: C, 65.51; H, 4.84; Fe, 30.10%).

The fourth band was eluted with 1/1 Skellysolve B/benzene to yield 0.28 g of material. This product was fractionally crystallized from Skellysolve B to yield a first set of crystals, 0.08 g (4%), of *meso* 1,2-quaterferrocene (X), m.p. 374—376°C (N_2)) with slow dec. starting at ca. 325°C; NMR ($CDCl_3$) singlet at δ 4.00 ($1'''$- and $1'''''$-protons), singlet at 4.28 ppm ($1'$- and $1'''''''$-protons); IR (KBr) 1100 and 995 cm^{-1} (unsubstituted cyclopentadienyl rings); mass spectrum *m/e* 738, calcd. mol. wt. 738. (Found: C, 65.34; H, 4.60; Fe, 30.50. $C_{40}H_{34}Fe_4$ calcd.: C, 65.09; H, 4.64; Fe, 30.26%).

The second set of crystals amounted to 0.08 g (4%) of *dl*-1,2-quaterferrocene (IX, m.p. 250—253°C dec. (N_2)); NMR ($CDCl_3$) multiplet at δ 3.82 (3H), singlet with underlying multiplet at 4.07 (12H, $1'$- and $1'''''''$ for the singlet), singlet with underlying multiplet at 4.22 (16H, $1'''$- and $1'''''$-protons for the singlet), multiplet at 4.55 ppm (4H); IR (KBr) 1102 and 993 cm^{-1} (unsubstituted cyclopentadienyl rings); mass spectrum *m/e* 738, calcd. mol. wt. 738. (Found: C, 65.11; H, 4.80; Fe, 30.20. $C_{40}H_{34}Fe_4$ calcd.: C, 65.09; H, 4.64; Fe, 30.26%).

Fractional crystallization from Skellysolve 8 of the material from the fifth band resulted in two sets of crystals. The first set of crystals produced 0.02 g (1%) of *meso*-1,2-quinqueferrocene (XI, m.p. 345—350°C (N_2)) with dec. starting about 270°C; IR (KBr) 1102 and 995 cm^{-1} (unsubstituted cyclopentadienyl rings); mass spectrum *m/e* 922, calcd. mol. wt. 922. (Found: C, 64.76; H, 4.84. $C_{50}H_{42}Fe_5$ calcd.: C, 65.13; H, 4.59%).

The second set of crystals amounted to 0.02 g (1%) of 1,2-quinqueferrocenes (XII and XIII, m.p. 180—230°C (N_2)) with foaming between 115—125°C; IR (KBr) 1102 and 995 cm^{-1} (unsubstituted cyclopentadienyl rings); mass spectrum *m/e* 922, calcd. mol. wt. 922.

Three additional bands were separated on the column which may have corresponded to the next three higher homologs of this series. However, only a few mg of each product per run was obtained, and they were not further investigated.

The yield results from other runs are summarized in Table 3.

TABLE 3

PERCENTAGE YIELDS OF 1,2-OLIGOMERIC FERROCENES[a]

Product Run	Run 1[b]	Run 2[b]	Run 3[c]	Run 4[c]
VI	31	33	3	1
III	11	17	3	1
IX	3	4	2	0.7
X	3	4	2	0.7
XI	1	1	1	0.4
XII and XIII	1	1	1	0.4

[a] Yields are based on the limiting reagent. [b] A 2/4 molar ratio of iodoferrocene to 1,2-diiodoferrocene was used. [c] No iodoferrocene; only 1,2-diiodoferrocene was used.

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