Formation of Ferrocene Oligomers from Mixed Ullmann Reactions of Halogenoferrocenes

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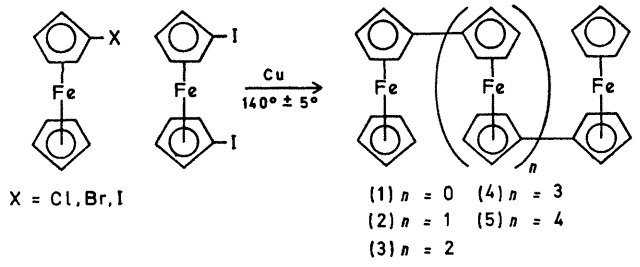
Summary The reactions of various halogenoferrocenes and 1,1′-di-iodoferrocene under Ullmann conditions result in the formation of ter-, quater-, quinque-, and sexiferrocene, these oligomeric ferrocenyls have been characterized by mass spectrometry

FERROCENE oligomers are of considerable current interest with regard to their thermal and conductivity properties [1–4] Moreover, the chemistry of polyferrocenes larger than biferrocenyl (**1**) is virtually unknown Terferrocene (**2**) has been obtained in low yield,[4–6] although only one report has appeared concerning higher homologues [6]

In connection with a programme designed to study the properties of oligomeric ferrocenes, we have recently developed an improved route to terferrocene (**2**), quaterferrocene (**3**), quinqueferrocene (**4**), and sexiferrocene (**5**), based on Ullmann biaryl reactions of halogenoferrocenes [7] Many of the reaction products have been characterized by elemental analysis and mass spectrometry (see Tables 1 and 2)



X = Cl, Br, I

(1) *n* = 0 (4) *n* = 3
(2) *n* = 1 (5) *n* = 4
(3) *n* = 2

TABLE 1

Percentage yields of ferrocene oligomers from mixed Ullmann reactions[a]

$FeC_{10}H_9X$	(1)	(2)	(3)	(4)	(5)
I	52	24	11	6	1
Br	35	29	9	4	2
Cl	71	11	10	6	2

[a] Reaction conditions 3 4 mmoles of halogenoferrocene, 6 8 mmoles of 1,1′-di iodoferrocene, and 0 17 mole of activated copper, heated at 140 ± 5° for 23 hours Yields are based on halogenoferrocene, and are reproducible

As is evident in Table 1, somewhat different product ratios were obtained depending on the halogenoferrocene used Iodoferrocene is known to be very reactive under Ullman conditions [7] and a substantial amount of the self-coupling product biferrocenyl (**1**) was obtained With bromoferrocene, mixed coupling with 1,1′-di-iodoferrocene

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evidently proceeds more rapidly than does self-coupling, and therefore the combined yield of the higher homologues (**2**)—(**5**) is greater than the yield of (**1**). The high yield of (**1**) formed in the reaction between chloroferrocene and 1,1′-di-iodoferrocene is surprising, since chloroferrocene exhibits a greatly diminished tendency to undergo Ullmann self-coupling.[7] This result may possibly be due to substantial rapid self-coupling of 1,1′-di-iodoferrocene, leaving chloroferrocene ultimately to couple with itself. In none of these reactions could the cyclic coupling product 1,1′-biferrocenylene[bis(fulvalene)di-iron][1,8] be detected.

TABLE 2

Properties of ferrocene oligomers from mixed Ullmann reactions

Oligomeric ferrocene[a]	m.p.[b]	lit. m.p.	M^+
Biferrocenyl (**1**)	238—240°	237—239[b,c]	370[d]
Terferrocene (**2**)	224—226	212·5—214·5[e] 226·5—227·2[f]	554[d]
Quaterferrocene (**3**)	279—281	280[f]	738[d]
Quinqueferrocene (**4**)	262—264	240—245[f]	922[g]
Sexiferrocene (**5**)	270—272	252—256[f]	1106[g]

[a] Each substance gave satisfactory carbon, hydrogen, and iron analyses. [b] Determined in sealed capillaries under nitrogen. [c] Ref. 7. [d] Determined on a Hitachi RMU-6E mass spectrometer at 70 ev. [e] Ref. 5. [f] Ref. 6. [g] Determined on an A.E.I. MS-9 mass spectrometer at 70 ev.

The mass spectra of each of the oligomeric ferrocenes (**1**)—(**5**) exhibit characteristic parent molecular ion peaks at the expected *m/e* values. In addition, M^{2+} peaks are observed in most of the spectra. These data as well as fragmentation patterns are in complete agreement with the suggested structures.

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