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RING MIGRATION IN ALKYLATED FERROCENES
II. SYNTHETIC APPLICATIONS

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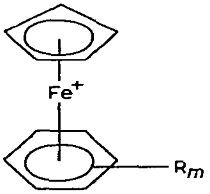
SUMMARY

A variety of isomeric polyethylated ferrocenes have been prepared and their behavior in (π-ligand)–(π-ligand) exchange reactions studied. IR and NMR correlations are presented for the intermediate ethylated acetylferrocenes and the polyethylated ferrocenes. Limitations upon the occurrence of ligand exchange reactions are discussed.

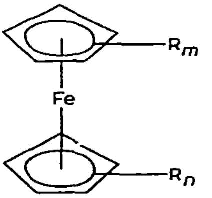
INTRODUCTION

Ligand exchange reactions in ferrocene and substituted ferrocenes have been the subject of numerous recent reports[1-5]. While detailed mechanistic studies are absent it has been established that (π-ligand)–(π-ligand) exchange is involved. The application of this reaction to the synthesis of a variety of compounds of the type (I) has been extensively studied by Nesmeyanov and coworkers[1,2,4-6].

In contrast, this reaction has not been investigated as a synthetic route to polyalkylated ferrocenes of the type (II).



(I)



(II)

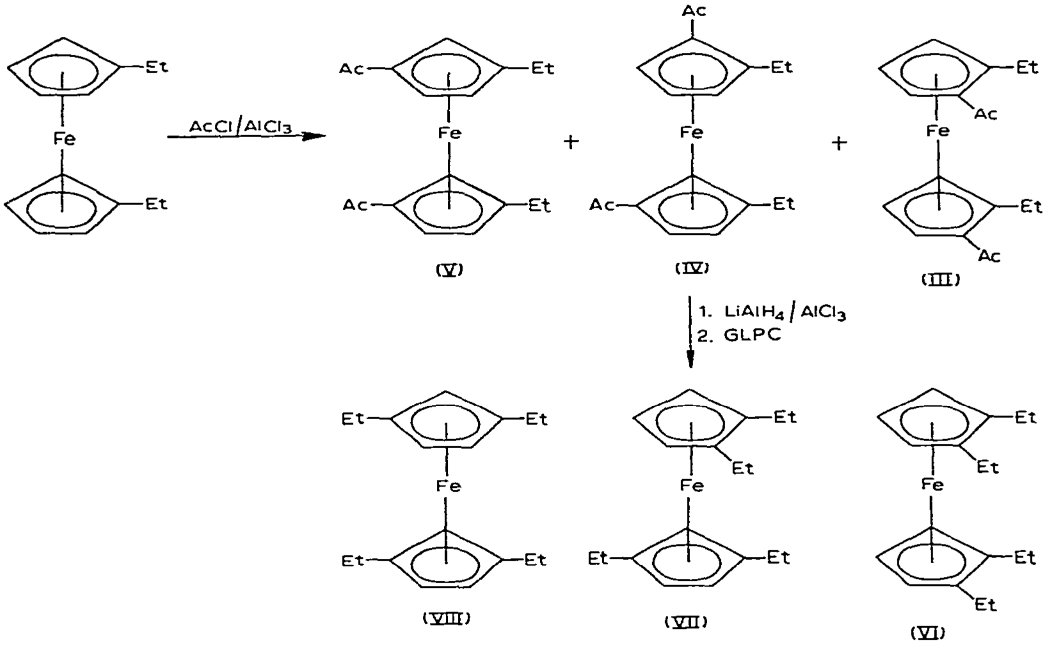
A comprehensive program to investigate the gas liquid partition chromatographic (GLPC) behavior and possible IR spectral correlations in tri-, tetra- and higher-substituted ferrocenes was undertaken. In this program ligand exchange reactions were anticipated as being an important synthetic tool. Thus, with a minimum of five appropriately polyalkylated ferrocenes, in addition to ferrocene itself, it is theoretically possible to synthesize the thirty-five isomeric alkylated ferrocenes in which the alkyl group remains constant.

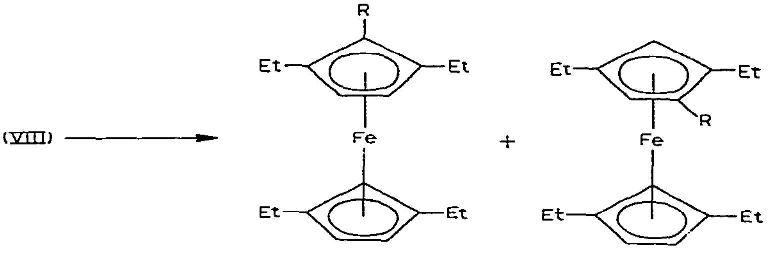
Isomeric acetylethylferrocenes and acetyldiethylferrocenes can be separated by column chromatography and identified with ease by their NMR and IR spectra[3,7-10]. Furthermore, the ready conversion of an acetyl group to an ethyl group[3,11] and the modest ease of separation of ethylated ferrocenes by GLPC[3,8,12-14] indicated polyethylated ferrocenes to be the compounds of choice for this study.

RESULTS AND DISCUSSION

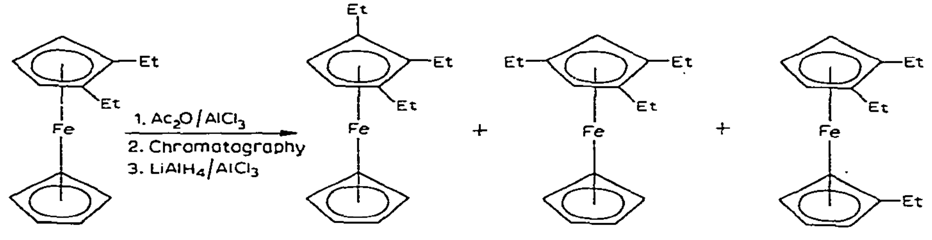
Synthesis

The general route employed in the present study for introduction of ethyl groups was that described earlier for the preparation of 1,2-diethylferrocene, 1,1',2- and 1,1', 3-triethylferrocene: acetylation of an ethylated ferrocene followed by chromatographic separation of the isomers and lithium aluminum hydride/aluminum chloride reduction to the pure isomeric ethylated ferrocenes. Thus, diacetylation of 1,1'-diethylferrocene produced a mixture of 2,2'-, 2,3'-, 3,3'-diethyl-1,1'-diacetylferrocene [(III), (IV), (V)] in an approximate ratio of 1/3/5. Subsequent reduction of this isomeric mixture by means of lithium aluminum hydride/aluminum chloride produced the corresponding 1,1',2,2'-, 1,1',2,3'- and 1,1',3,3'-tetraethylferrocenes [(VI), (VII), (VIII)] which were separated by preparative GLPC. Further monoacetylation of the last compound led ultimately to the formation of 1,1',2,3,3'- and 1,1',2,3',4-pentaethylferrocene [(IXb), (Xb)]. Similar reactions involving 1,2-diethyl- and 1,1',3-triethylferrocene provided pathways to authentic 1,2,3-, 1,2,4-triethylferrocene [(XI), (XII)] and 1,1',2,3-, 1,1',2,4-, 1,1',2,3'-tetraethylferrocene [(XIII), (XIV), (XV)] respectively.

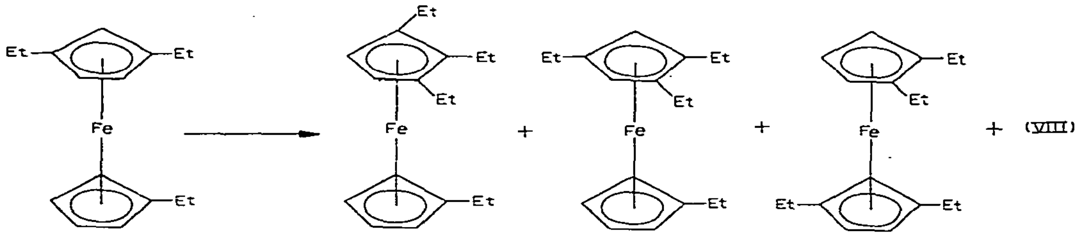




a, R = Ac; b, R = Et (IXa) (IXb) (Xa) (Xb)



(XI) (XII)



(XIII) (XIV) (XV)

Nonaethylferrocene and decaethylferrocene were prepared by the method of Schlögl[15]. Repeated alternate diacetylation of a mixture of 1,1′,2- and 1,1′,3-triethylferrocene followed by lithium aluminum hydride/aluminum chloride reduction led to a mixture of nona- and decaethylferrocene. Preparative GLC separation provided 0.5 g quantities of each of the desired products. Their structures were conclusively proven by their NMR spectra supplemented by their elemental composition. Nonaethylferrocene has a melting point of 181.5–185.0° while decaethylferrocene melts at 323–324°.

During the course of this study, it was found that previous correlations[3,7,9,10,16,17] between structure and ease of elution in column chromatographic separations applied equally well to these more highly substituted derivatives. The order of elution of the pure isomers from a mixture of acetylethylferrocenes is 1,2 > 1,1′ > 1,3. The difference between the last two isomers is small and their complete separation is difficult. Thus, in the present study, the most sterically crowded acetyl isomer was always the first to be eluted and readily separable from the other isomer(s). If both a second homoannular isomer and a heteroannular isomer were present their complete chromatographic separation was difficult to achieve. While it would have been desirable to obtain quantitative values for the acetylation ratios of the compounds studied, in most cases, it was impractical due to the incomplete separation of certain of the isomers.

Nuclear magnetic resonance spectra

NMR spectra of the compounds prepared in this study are summarized in Table 1. Structural assignments of the acetyl isomers of various ethylated ferrocenes are readily made when the previously-recognized effects of acyl and alkyl groups on adjacent cyclopentadienyl protons are considered[3,10,17–19]. In addition to the effects of an acetyl group on the cyclopentadienyl ring protons in those isomers where the acetyl group was adjacent to an ethyl group, there was a noticeable deshielding of the methylene protons but only a slight deshielding of the methyl protons. These observations are in agreement with those previously reported for the isomeric acetyl-1,1'-diethylferrocenes[3]. While the NMR spectra of isomeric acylated ferrocenes are sufficiently distinct to permit ready structural assignments, such is not the case for polyalkylated ferrocenes. In all the polyethylated ferrocenes examined cyclopentadienyl proton resonances occur as broad unresolved peaks in the region τ 6.00–6.23. Methylene and methyl proton resonances occur centered at τ 7.63–7.75 and τ 8.83–8.95 respectively. In certain of the individual compounds slight chemical shifts were apparent in the methylene region but they were of no consequence as an aid to struc-

TABLE 1

NMR PEAKS OF FERROCENE RING PROTONS[a]

Compounds	Chemical shifts (τ) and multiplicities[b] at ring positions								
	2	3	4	5	1'	2'	3'	4'	5'
1',2-diethyl-acetylferrocene		5.85 m	5.85 m	5.60 m		6.12 sb	6.12 sb	6.12 sb	6.12 sb
1',3-diethyl-acetylferrocene	5.53 m		5.80 m	5.53 m		6.12 sb	6.12 sb	6.12 sb	6.12 sb
2,3-diethyl-acetylferrocene[c]			5.73 d	5.53 d	6.03 s	6.03 s	6.03 s	6.03 s	6.03 s
3,4-diethyl-acetylferrocene[c]	5.38			5.38 s	6.02 s	6.02 s	6.02 s	6.02 s	6.02 s
1',2'-diethyl-acetylferrocene[c]	5.43 t	5.72 t	5.72 t	5.43 t			6.05 m	6.05 m	6.05 m
1',2,4-triethyl-acetylferrocene		5.80 d		5.63 d		5.95 m	5.95 m	5.95 m	5.95 m
1',2,3'-triethyl-acetylferrocene		5.82 m	5.82 m	5.60 m		6.13 m		6.13 m	6.13 m
1',3,3'-triethyl-acetylferrocene	5.57 m		5.83 m	5.57 m		6.20 m		6.20 m	6.20 m
1',2,3',5-tetraethyl-acetylferrocene		5.98 sb	5.98 sb			6.27 m		6.27 m	6.27 m
1',2,3',4-tetraethyl-acetylferrocene		5.97 d		5.80 d		6.30 m		6.30 m	6.30 m

[a] Determined on carbon tetrachloride solutions except as noted. [b] s = singlet, d = doublet, t = triplet, m = unresolved multiplet, sb = singlet, broad. [c] Deuteriochloroform solution.

tural assignment. In view of the recent articles by Schlögl and coworkers* regarding optically active ferrocenes it must be pointed out that most of the structures shown in Table 1 exist as *d,l* pairs. The structures throughout this text are not indicative of the absolute configurations.

Infrared spectra

The purpose of this study was to obtain a variety of polyethylated ferrocenes of known structure and examine their IR spectra to determine the applicability of previously established rules[21]. The value of the spectral region in the vicinity of 11 μ as a means of distinguishing between 1,2 and 1,3 orientations in substituted ferrocenes has been discussed by Rosenblum[21]. Examination of the data in Table 2 reveals all of the present derivatives containing a ring bearing only two ethyl groups in a 1,3 disposition exhibit the expected doublet of medium intensity peaks centered at 11.0 μ. An unexpected single peak of medium intensity at 7.95 μ is also present. The data also reveal that all those derivatives which contain a ring bearing only two ethyl groups in a 1,2 orientation exhibit a medium intensity doublet centered at 7.95 μ, a weak singlet at 14.7 μ and another located between 15.5–15.7 μ. While each of the compounds in the latter group did exhibit a single peak between 10.70–10.76 μ, the singlet referred to by Rosenblum, those derivatives which contain a monoethylated ring have in addition a single absorption at 11.1 μ.

TABLE 2

IR BANDS OF ETHYLATED FERROCENES[a]

Ferrocene compound	Region of spectral correlation (microns)[b]							
Ethyl	8.0 vw	9.09 s	10.1 s		11.1 m			16.0 vw
1,2	8.0 vw	9.09 s	10.07 s	10.74 m		14.80 w	15.64 w	
1,3	7.96 w	9.09 s	10.07 s		11.0 m(d)		15.88 vw	
1,1′	7.97 w	9.09 vw	9.86 s		11.1 m			16.13 w
1,2,3		9.02 s	10.0 s		11.0 m			
1,2,4		9.02 s	10.0 s	10.8 m				
1,1′,2	7.94 w		9.86 s	10.70 m	11.1 m	14.6 w	15.5 w	16.14 vw
1,1′,3	7.97 w		9.87s		11.0 m(d)			
1,1′,2,3	8.0 vw		9.92 s	10.77 w	11.2 m			
1,1′,2,4	8.0 vw		9.95 m	10.76 vw	11.0 m(d)			
1,1′,2,2′	8.0 vw			10.76 m		14.7 w	15.67 w	
1,1′,2,3′	7.97 w			10.76 w	11.0 m(d)	14.7 w	15.75 w	
1,1′,3,3′	7.97 w				11.0 m(d)		15.87 vw	
1,1′,2,3,3′	7.97 w		9.95 w	10.67 w	11.1 m(t)			
1,1′,2,3′,4	7.97 w			10.70 w	11.0 m(d)		15.88 vw	

[a] Determined in CS_2 solution. [b] Peak intensities (9, 10 μ arbitrarily assigned as strong) s = strong, m = medium, w = weak, vw = very weak, d = doublet, t = triplet.

While spectral distinctions exist between isomers having a 1,2 or 1,3 orientation no correlations were found which would allow one to distinguish between 1,2,3 and 1,2,4 dispositions. The spectra in each of these classes are somewhat self-consistent

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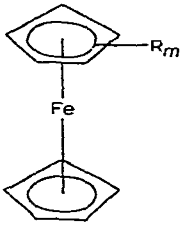
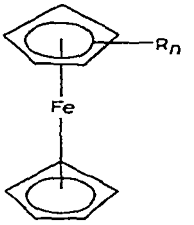
* For leading references see ref. 20.

and distinct among themselves but there exists no omnipresent significant peak(s) which will permit distinction between the two classes without reference scans.

The IR spectra of substituted ferrocenes of the type (II) have been observed to be almost identical to a composite spectrum obtained by adding the spectra of the respective ferrocenes (XVI) and (XVII) and subtracting those peaks attributable to



(XVI)



(XVII)

the unsubstituted ring. This additivity principle has been found to apply to numerous substituted ferrocenes. In the past this has been found to be valid for substituted ferrocenes containing up to two substituents in a ring. The number of polyethylated ferrocenes of known orientations available in this study suggested an examination of the validity of the application of the additivity principle to trisubstituted systems. Throughout this entire study the application was found to be valid. While most spectra are quite close to what might be expected, on the basis of additivity, the spectrum of 1,1′,2,3,3′-pentaethylferrocene has some deviations from a composite of 1,2,3-triethyl- and 1,3-diethylferrocenes.

Examination of the spectra of the polyethylated ferrocenes in the region from 16–35 μ indicated there was no correlation between orientation and absorption in this region.

Correlations noted in the IR spectra of certain intermediate polyethylated acetylferrocenes in general agreed with those previously reported for acylalkylferrocenes[21]. However, there appeared to be more latitude in the position of the characteristic peaks in the various spectra. In contrast to most 1,3-acylalkylferrocenes, which absorb at 10.85 and 11.05 μ, 4-acetyl-1,2-diethylferrocene absorbs at 10.93 and 11.14 μ. Similarly 3-acetyl-1,2-diethylferrocene absorbs at 11.11 μ while 1,2-disposed acylalkylferrocenes usually absorb at 10.90 μ. As a result of this wider variation and consequent lower reliability structural assignments were based upon the more definitive NMR spectra of the various ethylated acetylferrocenes. The structures of the various polyethylated ferrocenes rest firmly upon their well characterized acetyl precursors.

Gas liquid partition chromatographic analyses

GLPC analyses of the various polyethylated ferrocenes revealed that the [illegible] of di-, tri- or tetrasubstituted ferrocenes as

TABLE 3

RELATIVE RETENTION TIMES AND BOILING POINTS OF POLYETHYLATED FERROCENES[a]

Position of ethyl group	Relative retention time[b]	B.p. [°C(mm)]	n_D^{25}
1	1.00	263(760)	1.5968
1,2	1.45	287(760)	1.5764
1,3	1.37	283(760)	1.5753
1,1′	1.37	283(760)	1.5768
1,2,3	2.06	310(760)	1.5630
1,2,4	1.79	303(760)	1.5609
1,1′,2	1.97	302(764)	1.5630
1,1′,3	1.81	299(764)	1.5628
1,1′,2,3	2.55		
1,1′,2,4	2.26	316(764)	1.5508
1,1′,2,2′	2.56	319(764)	1.5517
1,1′,2,3′	2.35	314(761)	1.5540
1,1′,3,3′	2.14	307(764)	1.5490
1,1′,2,3,3′	3.01	332(764)	1.5482
1,1′,2,3′,4	2.64	323(764)	1.5468

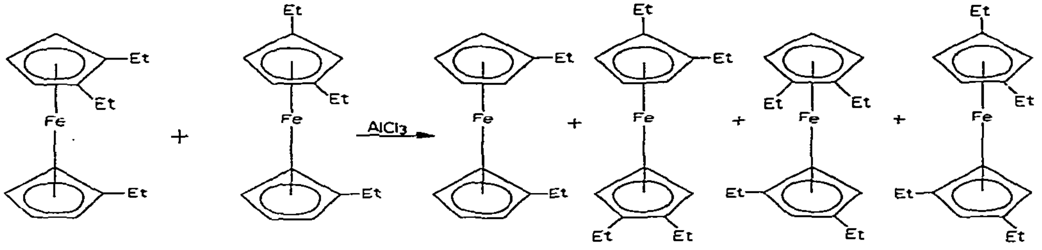
[a] Determined on 20′-20% Apiezon L on 60/80 chromosorb P at 290°. [b] Retention time of compound from air relative to normalized internal standard of ethylferrocene.

to note that to all outward appearances the 1,1′ orientation in dialkylferrocenes is very nearly identical to the 1,3 orientation in terms of steric effects manifested in the boiling points of these compounds. This can be seen by comparing the boiling points of 1,1′-diethylferrocene with the 1,3 isomer and 1,2,4-triethylferrocene with the 1,1′,3 isomer.

Ring migration studies

After nonaethylferrocene was treated with aluminum chloride in refluxing methylene chloride, GLPC analysis demonstrated the presence of only nonaethylferrocene after normal workup of the reaction mixture. Thus, while nonaethylferrocene forms a highly colored complex with aluminum chloride in methylene chloride, this complex either does not disproportionate or does so at an exceedingly slow rate. Similar attempts to prepare 1,2,3,4-tetraethyl- and 1,2,3,4,5-pentaethylferrocene by synproportionation of nonaethylferrocene with ferrocene were unsuccessful. Attempted synproportionation of ferrocene and decaethylferrocene led only to recovered starting materials.

It has previously been shown that either 1,1′,2- or 1,1′,3-triethylferrocene disproportionates to 1,1′-di- and 1,1′,2,2′-tetraethylferrocene or 1,1′-di- and 1,1′,3,3′-tetraethylferrocene respectively[3]. Disproportionation of a mixture of 1,1′,2- and 1,1′,3-triethylferrocene produced, in addition to the above products, 1,1′,2,3′-tetraethylferrocene (VII) identified by comparison of its IR spectrum with that of an observed. Attempted disproportionations of 1,1',2,3'-tetraethylferrocene were similarly unsuccessful in the presence of aluminum chloride in methylene chloride or neat with aluminum chloride. These facts when taken together indicate a complex reaction to be occurring when a mixture of 1,1',2 and 1,1',3 triethylferrocene is reacted with aluminum chloride as shown below:



(XVIII) (XIX) (VI) (VII) (VIII)

$$\text{(XIX)} + \text{(VI)} + \text{(VIII)} \xrightarrow{AlCl_3} \text{(XVIII)} + \text{(XIX)} + \text{(VII)}$$

$$\text{(VI)} + \text{(VIII)} \underset{\not\leftarrow}{\xrightarrow{AlCl_3}} \text{(VII)}$$

Thus, while 1,1',2,2' and 1,1',3,3'-tetraethylferrocene [(VI) and (VIII)] each synproportionate with ferrocene such is not the case with the 1,1',2,3' isomer.

The phenomenon of ring migration in ethylated ferrocenes is apparently affected by the number of ethyl groups present. In order to determine the limitations of this reaction 1,2,4- and 1,2,3-triethylferrocene, 1,1',2,4-tetraethylferrocene and 1,1',2,3',4-pentaethylferrocene were submitted to the conditions of ring migration. No ring migration was found to have occurred when 1,1',2,3',4-pentaethylferrocene was contacted with aluminum chloride in refluxing methylene chloride. However, when the reaction was carried out neat at 100° for seven hours there was observed a mixture of 86% starting material, 4% of compound (VIII) and 10% 1,1',2,2',4,4'-hexaethylferrocene. The latter material was identified as a hexaethylferrocene by its mass spectrum and as the 1,1',2,2',4,4' isomer by its IR spectrum which was almost identical to 1,2,4-triethylferrocene less the unsubstituted ring absorptions. Further evidence was the general resemblance of its IR spectrum to known compounds containing 1,2,4 orientations. There was no resemblance to the known 1,2,3 isomers.

1,1',2,4-Tetraethylferrocene (XIV) was heated for one hour at 100° in the presence of aluminum chloride. Analysis (GLPC) indicated the presence of 1,1',2,2',4,4'-hexaethylferrocene and 1,1'-diethylferrocene as evidenced by their GLPC retention times and IR spectra. In addition to the ring migration products there were also noticeable amounts of dealkylation products (see Table 4). Treatment of either 1,2,3- or 1,2,4-triethylferrocene with aluminum chloride, neat, at 100° produced, in each case, both ring migration and a variety of dealkylation products. GLPC analysis of the 1,2,3-triethylferrocene reaction mixture revealed the presence of ethylferrocene and 1,2-diethylferrocene. No 1,3-diethylferrocene was observed indicating preferential loss of the 1, or 3 ethyl group. In contrast, the dealkylation products of 1,2,4-triethylferrocene (XII) were 1,2- and 1,3-diethylferrocene and ethylferrocene. The retention times of the various ethylated ferrocenes are tabulated in Table 3. The retention times

TABLE 4

RING MIGRATION PRODUCTS OF ETHYLATED FERROCENES[a]

Orientation of products (%)[b,c]	Orientation of starting materials[c]					
	1,2,3	1,2,4	1,1',2 + 1,1',3	1,1',2,3'	1,1',2,4	1,1',2,3',4[d]
Ferrocene	5	4				
Ethylferrocene	7	5	1			
1,2	2	4				
1,1'	1[e]	5[e]	21		3	
1,2,3	21					
1,2,4		16[f]				
1,1',2		[g]	16		3	
1,1',3	2	16	36		4[h]	
1,1',2,4		15			61	
1,1',2,2'	9[i]	[g]	7			
1,1',2,3'		[g]	13	*ca.* 98		
1,1',3,3'		[g]	6			4
1,1',2,2',3	12					
1,1',2,2',4		14			9	
1,1',2,3',4		12			9	86
1,1',2,2',3,3'	40					
1,1',2,2',4,4'		18			11	10

[a] All reactions were carried out neat, unless otherwise stated. [b] Not corrected for differences in thermal conductivity of the various products. [c] Attempted disproportionation of nonaethylferrocene (in CH_2Cl_2) and synproportionation of ferrocene + 1,1',2,3' (neat), 1,1' + 1,1',2,3',4 (in CH_2Cl_2), ferrocene + 1,1',2,3',4 (in CH_2Cl_2) and ferrocene + decaethylferrocene (in CH_2Cl_2) led only to recovered starting materials. [d] 6 h at 100°. [e] Not distinguished from 1,3 isomer. [f] In addition there was 5% of unknown at rel. ret. time 1.91. [g] Trace. [h] Not distinguished from 1,2,4 isomer. [i] Not distinguished from 1,1',2,3 isomer.

are relative to an internal standard of air and normalized to ethylferrocene.

Analysis (GLPC) of the intermediate mixed polyethylated ferrocenes, which served as intermediates to the decaethylferrocene, demonstrated that the major component of the mixed pentaethylferrocenes could be assigned as 1,1',2,3',4-pentaethylferrocene. Comparison of the IR scan of a small preparative GLPC sample to that of authentic material confirmed its identity. The formation of this isomer as the major component could be predicted on the basis that diacetylation of a mixture of 1,1',2- and 1,1',3-triethylferrocene in which the last isomer predominates would give the least hindered 3',4-diacetyl-1,1',3-triethylferrocene as the major product. Similarly the 1,1',2-isomer would give the less hindered 3',4-diacetyl-1,1',2-triethylferrocene as the major product. Upon reduction to the pentaethylferrocene, these two products form the same 1,1',2,3',4-pentaethylferrocene thus mutually reinforcing the predominance of this isomer. The combined less sterically favored diacetyl isomers upon reduction comprise the remaining three isomeric pentaethylferrocenes having retention times of 2.94, 3.05 and 3.38. The materials were identified as 1,1',2,2',4-pentaethylferrocene (tentative), respectively. The first and third compounds were tentatively assigned on the basis of their resemblances to expected composite spectra and the family of spectra having known 1,2,4 and 1,2,3 orientations. The IR spectrum of the 1,1',2,3',4 isomer was identical to that of authentic material prepared by reduction of 1-acetyl-1′,2,3′,4-tetraethylferrocene.

The data obtained indicate that ring migration in polyethylated ferrocenes occurs readily as indicated by disproportionation and synproportionation reactions for all isomers containing up to three ethyl groups. When more than three ethyl groups are present this generalization no longer holds and one must examine each case individually. Thus, within the series of tetraethylated ferrocenes studied the 1,1′,2,2′ and 1,1′,3,3′ isomers undergo ring migration with trace dealkylation, the 1,1′,2,4 isomer undergoes ligand exchange with greater amounts of dealkylation products evident, and the 1,1′,2,3′ isomer is recovered unchanged. The only pentaethylferrocene studied undergoes both ring migration and dealkylation. Immunity to ligand exchange, under the reaction conditions employed, is exhibited by both nona- and decaethylferrocene.

EXPERIMENTAL

IR spectra were determined on a Beckman Model IR-10 IR spectrophotometer, NMR spectra were determined using a Varian Model A-60 spectrometer and mass spectra on an Atlas CH-4. Boiling point determinations were conducted on a DuPont Model 900 differential thermal analyzer. Gas–liquid partition chromatographic analyses were performed on an Aerograph Autoprep Model A-700 equipped with a $\frac{3}{8}$ in x 20 ft aluminum column packed with Apiezon L (20%) on 60/80 chromosorb P.

Preparation of 1,1′,2,2′-, 1,1′,2,3′- *and* 1,1′3,3′-*tetraethylferrocene*

To a stirred solution of 4.8 g (0.02 mole) 1,1′-diethylferrocene in 100 ml dry methylene chloride in a nitrogen atmosphere was added, over a period of 5 min, a solution containing 4.0 g (0.03 mole) aluminum chloride and 2.4 g (0.03 mole) acetyl chloride in 100 ml dry methylene chloride. The reaction mixture was refluxed for 2 h then cooled and poured over ice. The organic layer was separated and dried with anhydrous magnesium sulfate then evaporated *in vacuo*. The residual red oil (5.1 g) was dissolved in 100 ml dry ether and added dropwise with stirring to a previously prepared solution of 3 g lithium aluminum hydride and 9.0 g aluminum chloride in 200 ml ether. The reaction mixture was maintained at reflux for 2 h then cooled and carefully hydrolyzed. The organic phase was separated, dried over anhydrous magnesium sulfate and evaporated to dryness. The residual oil was analyzed by GLPC and found to consist of trace amounts of 1,1′-diethyl, 1,1′,2- and 1,1′,3-triethylferrocene in addition to 1,1′,3,3′-, 1,1′,2,3′- and 1,1′,2,2′-tetraethylferrocene in the amounts 55, 36 and 8%, respectively. The structures of the 1,1′,3,3′ and 1,1′,2,2′ isomers were proven by the identity of their IR spectra and GLPC retention times with those of authentic compounds[3]. Preparative GLPC of the reaction mixture provided samples of each of the pure isomeric tetraethylferrocenes. The structure of the previously unknown 1,1′,2,3′-tetraethylferrocene thus obtained was proven by the identity of its IR spectrum with that of a sample prepared by the reduction of 1-acetyl-1′,2,3′-triethylferrocene (see below) in addition to its microanalytical data. (Found: C, 72.67; H, 8.73. $C_{18}H_{26}Fe$ calcd.: C, 72.48; H, 8.79%.)

Preparation of 1,1′,2,3,3′- *and* 1,1′,2,3′,4-*pentaethylferrocene*

To a stirred solution of 1.33 g 1,1′,3,3′-tetraethylferrocene in 100 ml dry methylene chloride in a dry nitrogen atmosphere was added dropwise a solution of 0.65 g aluminum chloride and 0.39 g acetyl chloride in 75 ml dry methylene chloride. The reaction mixture was stirred at reflux for 2 h then cooled and poured over ice. The organic layer was separated, dried, and evaporated to dryness *in vacuo*. The residue was dissolved in hexane and chromatographed on a column of activity grade III alumina (Alcoa-F20). Elution with hexane removed a trace of unchanged starting material. Elution with 2% ether/hexane provided, after removal of the solvent, a red oil (*ca.* 0.1 g) identified as 1-acetyl-1′,2,3′,5-tetraethylferrocene by means of its NMR spectrum (Table 2). Continued elution with 2% ether/hexane removed 0.6 g of a second material identified by means of its NMR spectrum as 1-acetyl-1′,2,3′,4-tetraethylferrocene. Reduction of each of the above isomers by an excess of lithium aluminum hydride/aluminum chloride provided the corresponding 1,1′,2,3,3′-and 1,1′,2,3′,4-pentaethylferrocenes. (Found: C, 73.73; H, 9.25. $C_{20}H_{30}Fe$ calcd.: C, 73.61; H, 9.27%.)

Insufficent sample of the 1,1′,2,3,3′ isomer was obtained for analyses other than an IR spectrum and relative retention time.

Preparation of 1,3-*diethylferrocene*

To a stirred solution of 1.0 g lithium aluminum hydride and 3.0 g aluminum chloride in 100 ml dry ether was added dropwise a solution of 0.25 g 1-acetyl-3-ethylferrocene[7], whose structure was confirmed by its NMR spectrum, in 20 ml ether. After 2 h at reflux, the reaction mixture was worked up as above to provide a quantitative yield of 1,3-diethylferrocene. (Found: C, 68.90; H, 7.43. $C_{14}H_{18}Fe$ calcd.: C, 69.43; H, 7.50%.)

Preparation of 1,2,3- *and* 1,2,4-*triethylferrocene*

To stirred solution of 2.3 g 1,2-diethylferrocene[3] in 100 ml dry methylene chloride was added dropwise, in a nitrogen atmosphere, a solution containing 1.5 g acetic anhydride and 3.7 g aluminum chloride in 100 ml dry methylene chloride. After the normal work up procedure the residual red oil was taken up in hexane and chromatographed on a column of activity grade III alumina. Elution with hexane removed 0.17 g recovered starting material. Elution with 2% ether/hexane removed a trace of an unidentified material. When the eluent was changed to 5% ether/hexane there was obtained 0.5 g of a red oil identified as 1-acetyl-2,3-diethylferrocene by means of its NMR spectrum. Elution with 5% ether/hexane was continued until the eluate again became colored. At this point the column was cut into six segments of equal length and the adsorbent in each exhaustively extracted with ether. Analysis (NMR) of the materials removed demonstrated the bottom three segments to contain pure 1-acetyl-1′,2′-diethylferrocene the fourth segment contained a mixture of the 1′,2′- and 2,4-diethylacetylferrocene. The two remaining segments were found to contain pure 1-acetyl-2,4-diethylferrocene.

Each of the pure isomeric acetyl-1,2-diethylferrocenes was reduced by lithium aluminum hydride/aluminum chloride to provide 1,2,3-triethylferrocene (0.42 g), 1,2,4-triethylferrocene (0.43 g) and 1,1′,2-triethylferrocene (1.14 g). The latter material was identical in all respects to an authentic sample. [Found (1,2,3 isomer): C, 70.8;

H, 8.3. Found (1,2,4 isomer): C, 71.6; H, 8.3. $C_{16}H_{22}Fe$ calcd.: C, 71.12; H, 8.21%.)

Preparation of 1,1',2,4-*tetraethylferrocene*

A solution of 4.1 g 1,1',3-triethylferrocene was monoacetylated using 1 molar equivalent of aluminum chloride, acetic anhydride in methylene chloride. The reaction product was placed on a column of activity grade III alumina and eluted with hexane to remove unchanged starting material. Elution with 2% ether/hexane removed a band which was taken off in two fractions. NMR analysis of each cut showed the first fraction was composed of 1',2,5- and 1',2,3'-triethylacetylferrocene in an approximate ratio of 2/1. Rechromatography of each fraction provided the pure isomers.

When the eluent was changed to 10% ether/hexane a second band was removed. The NMR spectrum demonstrated it to be 1-acetyl-1',3,3'-triethylferrocene. Upon reduction 1-acetyl-1',2,3'-triethylferrocene provided 1,1',2,3'-tetraethylferrocene identical to that obtained from diacetylation of 1,1'-diethylferrocene followed by reduction. Reduction of the isomeric 1',2,5- and 1',2,4-triethylacetylferrocenes produced the respective 1,1',2,3- and 1,1',2,4-tetraethylferrocenes. A sufficient amount of the former material was obtained only for an IR spectrum and relative retention time. Analysis of the latter material by GLPC showed it to be free of any contamination.

Preparation of nona- and decaethylferrocene

The procedure was identical to that of Schlögl[15], however, after the final step in order to obtain pure materials GLPC (5'-5% Apiezon L, 285°) was necessary. The nonaethylferrocene thus obtained (m.p. 181.0–185.0) exhibited proton resonances, in carbon tetrachloride, at τ 6.80 (1 H), τ 7.83 (17.4 H) and τ 8.96 (26.4 H). (Found, C, 76.32; H, 10.89. $C_{28}H_{46}Fe$ calcd.: C, 76.66; H, 10.57%.)

Decaethylferrocene sublimes readily at elevated temperatures and decomposes at its melting point. The best value obtained was 323–324°. Its NMR spectrum consisted of a triplet centered at τ 8.96 (3 H) and a quartet centered at τ 8.67 (1.98 H).

Ring migration studies

The disproportionation and synproportionation reactions were performed in the manner described earlier[3] or by heating neat in the presence of aluminum chloride for 2 h at 100° in a vessel protected from the air. The reactions were quenched with water and the reaction products analyzed by GLPC. The results are listed in tabular form in Table 4. The various products were characterized by comparison of their IR spectra and relative retention time with those of authentic materials. Tentative structural assignments for certain of the compounds based solely on IR and estimated relative retention times are indicated in the table.

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