

624. *Ferrocene Derivatives containing Tertiary Alkyl Groups. Synthesis by the Friedel-Crafts and Other Methods.*

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Contrary to a previous report, the alkylation of ferrocene with *t*-butyl chloride under Friedel-Crafts conditions proceeds smoothly, and mono-, 1,1'-di-, 1,3-di-, 1,1',3-tri-, and 1,1',3,3'-tetra-*t*-butylferrocenes can be isolated crystalline. 1,1'-Di-*t*-alkylferrocenes are also prepared from the corresponding *t*-alkylcyclopentadienes, which are obtained by treating cyclopentadienylmetal halides with *t*-alkyl halides. Alkylferrocenes containing *t*-alkyl groups separated from the nucleus by one and two carbon atoms are described. From the reaction between pivaloyl chloride and ferrocene in the presence of aluminium chloride various products, including 1,1'-dipivaloyl-3,3'-di-*t*-butylferrocene, are obtained. A synthesis of neopentylcyclopentadiene *via* ethoxymethylcyclopentadiene is recorded.

ALKYL derivatives of cyclopentadiene have been used for the preparation of the corresponding 1,1'-dialkylferrocenes.¹ By treating cyclopentadienyl-sodium or -potassium in either liquid ammonia or organic solvents with *n*- and *s*-alkyl halides the alkylcyclopentadienes are obtained in high yield² but attempts to prepare *t*-butylcyclopentadiene from cyclopentadienyl-sodium, -lithium, or -potassium and *t*-butyl chloride were unsuccessful. Riemschneider and Grabitz³ could not make cyclopentadienylpotassium react with *t*-butyl bromide, and similar failures to cause reaction between *t*-butyl chloride and other organosodium compounds have been reported. Homeyer *et al.*⁴ could not alkylate malonic ester, and Hamrick *et al.*⁵ noted the absence of reaction between sodium diphenylmethide and *t*-butyl chloride. In contrast to these findings, a recent German patent⁶ claims 50–80% yields of *t*-alkylcyclopentadienes from cyclopentadienylsodium and *t*-alkyl bromides. It has been found by the author, and independently by Riemschneider and Nehring,⁷ that if the alkali-metal derivative of cyclopentadiene is replaced either by a cyclopentadienyl-magnesium halide or by cyclopentadienylzinc chloride, then alkylation with *t*-alkyl chlorides is readily effected. The *t*-alkylcyclopentadienes listed in Table 1 were all prepared from

¹ B.P. 733,129.

² Alder and Holzrichter, *Annalen*, 1936, **524**, 145; B.P. 763,825.

³ Riemschneider and Grabitz, *Monatsh.*, 1958, **89**, 748.

⁴ Homeyer, Wallingford, and Whitmore, *J. Amer. Chem. Soc.*, 1933, **55**, 4209.

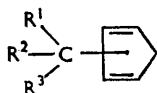
⁵ Hamrick and Hauser, *J. Amer. Chem. Soc.*, 1957, **79**, 3142.

⁶ D.A.S. 1,110,635.

⁷ Riemschneider and Nehring, *Monatsh.*, 1959, **90**, 568.

cyclopentadienylmagnesium bromide and the appropriate t-alkyl chlorides. The latter differ appreciably in their reactivity towards the Grignard reagent; t-butyl chloride reacted slowly at 25°, and 2-chloro-2,4,4-trimethylpentane reacted vigorously at 0°. An alternative procedure for the preparation of t-butylcyclopentadiene from dimethylfulvene and methyl-lithium has been described by Knox and Pauson.⁸

TABLE 1.
t-Alkylcyclopentadienes, C₅H₅·CR¹R²R³.



R ¹	R ²	R ³	B. p.	Yield (%)	
Me	Me	Me	45°/28 mm.	66	(I)
Me	Me	Et	40/10	67	(II)
Me	Et	Et	40/4	66	(III)
Me	Me	Pr ⁿ	24/0·5	68	(IV)
Me	-[CH ₂] ₅ -		40/0·5	32	(V)
Me	Me	CH ₂ ·CMe ₃	37/0·1	35	(VI)

t-Alkylcyclopentadienes proved to be much more resistant to polymerisation than cyclopentadiene itself. They were converted into their sodium derivatives either by treatment with sodium in liquid ammonia or with finely dispersed sodium in tetrahydrofuran. By treating the sodium derivatives with ferrous chloride the I, I'-di-t-alkylferrocenes were obtained, and these are listed in Table 2. The first member of this series has been

TABLE 2.
I, I'-Di-t-alkylferrocenes.

From	M. p.	Yield (%)	Formula	Analysis					
				Found (%)			Required (%)		
				C	H	Fe	C	H	Fe
(I)	28°	61	C ₁₈ H ₂₆ Fe	72·4	8·4	19·5	72·5	8·7	18·8
(II)	0	57	C ₂₀ H ₃₀ Fe	74·2	9·3	16·9	73·7	9·2	17·2
(III)	34	50	C ₂₂ H ₃₄ Fe	75·2	9·8	15·9	74·6	9·6	15·8
(IV)	21	48	C ₂₂ H ₃₄ Fe	75·1	9·9	16·1	74·6	9·6	15·8
(V)	67	45	C ₂₄ H ₃₄ Fe	76·5	8·4	15·0	76·2	9·0	14·8
(VI)	48	57	C ₂₆ H ₄₂ Fe	76·5	10·4	13·7	76·1	10·3	13·7

described by Knox and Pauson⁸ and by Riemschneider and Nehring.⁷ The former workers obtained the dialkylferrocene by treating the adduct of dimethylfulvene and methyl-lithium with ferrous chloride, and at about the same time Koestler and Little⁹ reported similar syntheses of heteroannular disubstituted ferrocenes from fulvenes.

With acyl halides and aluminium chloride as catalyst, ferrocene readily yields mono- and di-acyl derivatives, and these may be reduced to the corresponding alkylferrocenes, but attempts to alkylate ferrocene directly under Friedel-Crafts conditions have given disappointing results. Helm and Riemschneider¹⁰ were unable to alkylate ferrocene with ethyl bromide, isopropyl chloride, and benzyl chloride, and Rausch *et al.*¹¹ reported the formation of mixtures of liquid alkylferrocenes, none of which could be isolated as pure compounds either by distillation or by chromatography. Nesmeyanov and Kotchetkova¹² obtained 20–30% yields of mixtures of alkylation products with ethyl bromide, n-butyl chloride, and benzyl chloride and reported the isolation, by distillation, of mono-, di-, and penta-alkylated ferrocenes in very small yield. In a subsequent Paper¹² these authors

⁸ Knox and Pauson, *Proc. Chem. Soc.*, 1958, 289; *J.*, 1961, 4610.

⁹ Koestler and Little, *Chem. and Ind.*, 1958, 1589; *J. Org. Chem.*, 1961, **26**, 3247.

¹⁰ Helm and Riemschneider, *Chem. Ber.*, 1956, **89**, 155.

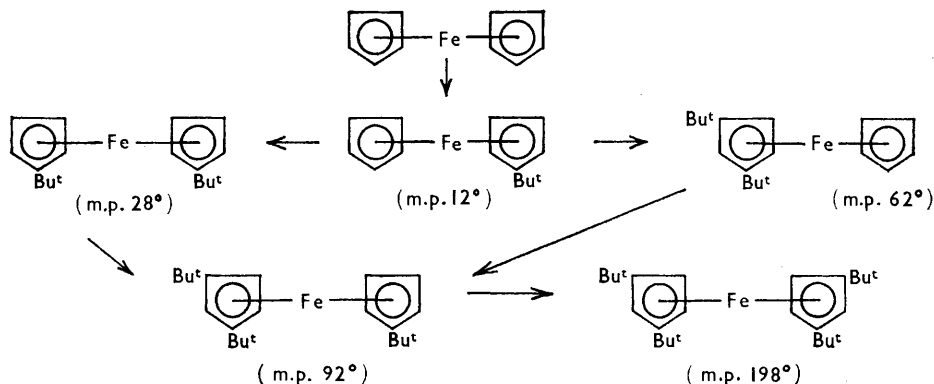
¹¹ Rosenberg, Rausch, and Vogel, *J. Org. Chem.*, 1957, **22**, 1016.

¹² Nesmeyanov and Kotchetkova, *Doklady Akad. Nauk S.S.S.R.*, 1956, **109**, 543; 1957, **114**, 800; 1957, **117**, 92.

claim to have isolated mono- and di-*t*-butylferrocenes in small yield as liquids of b. p.s 103—105°/4 mm. and 124—125°/3 mm., respectively. From infrared adsorption measurements they conclude that the di-*t*-butylferrocene contains one unsubstituted cyclopentadiene ring. Paushkin *et al.*¹³ also claim to have prepared mono- and di-*t*-butylferrocenes from ferrocene and isobutene, and, like the previous authors, they deduce from the infrared adsorption that the dibutylferrocene is the homo-annular derivative. Further attempts to alkylate ferrocene with *t*-butyl alcohol in the presence of Friedel-Crafts catalysts were made by Neuse and Trifan¹⁴ who reported the production of low yields of reddish-brown oils. Good yields of aralkylferrocene derivatives were, however, obtained from α -aryl alcohols, and the structures of these ferrocene derivatives were confirmed by alternative syntheses.

The above results were confirmed in experiments with *n*- and *s*-alkyl halides but it was found that alkylation with *t*-butyl chloride may be readily effected in the presence of Friedel-Crafts catalysts to give high yields of mixtures of *t*-butylferrocenes. No difficulty was experienced in the resolution of these mixtures, and the course of the alkylation is indicated below. The identities of the poly-*t*-butylferrocenes were established as follows. Mono-*t*-butylferrocene was prepared by treating an equimolecular mixture of the sodium derivatives of cyclopentadiene and *t*-butylcyclopentadiene with ferrous chloride. The resulting mixture of mono-*t*-butyl-, 1,1'-di-*t*-butyl-, and unsubstituted ferrocene was resolved by chromatography on alumina. Alkylation with *t*-butyl chloride of either of the isomeric di-*t*-butylferrocenes of m. p.s 28 and 62° gave a high yield of the same tri-*t*-butylferrocene of m. p. 92°, and this in turn was further alkylated to give a single tetra-*t*-butylferrocene. Assuming that the *t*-alkyl groups will not attach themselves to adjacent carbon atoms it follows that the *t*-butylferrocenes will have the formulae assigned.

Mixtures of *t*-butylferrocenes of varying composition were obtained by varying the alkylation conditions. The mixtures were easily separated either by fractional distillation or by chromatography on alumina. Except for the preparation of the otherwise difficultly accessible 1,3-disubstituted derivative, the reaction is of little value for the preparation of mono-, and 1,1'-di-*t*-butylferrocenes, and the latter is best prepared from *t*-butylcyclo-



pentadiene. It was not possible to stop the reaction at the first stage; alkylation with one molecule of *t*-butyl chloride gave a product which consisted of a mixture of unchanged ferrocene, *t*-butylferrocene, 1,1'- and 1,3-di-*t*-butylferrocenes, and a small amount of 1,1',3-tri-*t*-butylferrocene. It is interesting to note that the homoannular and heteroannular disubstituted ferrocenes are formed in approximately the ratio 1 : 4. The rates of formation of 1,1',3-tri- and 1,1',3,3'-tetra-*t*-butylferrocenes proved to be markedly different,

¹³ Paushkin, Vishnyakova, and Sokolinskaya, *Neftekhimiya*, 1963, **3**, 280 (*Chem. Abs.*, 1963, **59**, 6438).

¹⁴ Neuse and Trifan, *J. Amer. Chem. Soc.*, 1962, **84**, 1850.

and by adjusting the reaction conditions either one of these could be obtained pure in over 60% yield from ferrocene. They were readily purified simply by crystallisation from alcohol, in which the tetra-substituted ferrocene is only sparingly soluble.

Alkylations were done in the presence of both anhydrous aluminium chloride and zinc chloride. With the latter, higher temperatures were necessary. Alkylations with *t*-butyl chloride in the presence of aluminium chloride were done at 5–15°. At higher temperatures this catalyst caused isomerisation of the alkyl groups. A further example of this effect was obtained by heating 1,1'-di-*t*-pentylferrocene with 0.3 mol. of aluminium chloride at 70° for 3 hours when a mixture of three isomeric dipentylferrocenes was produced. Choice of solvent was found to be important; a wide variety of solvents were tried, and excellent yields were obtained with the halogenated hydrocarbons, *n*-butyl chloride, ethylene dichloride, methylene dichloride and tetrachloroethane. Poor results were obtained when carbon disulphide, nitrobenzene, and nitromethane were used as solvents. The progress of the reaction was usually determined by measuring the quantity of hydrogen chloride evolved. The first molecule of hydrogen chloride remained combined with the ferrocene-aluminium chloride complex and was not liberated from the reaction mixture.

As stated above, a convenient method for the introduction into the ferrocene nucleus of either one or two alkyl groups of the general formula $-\text{CH}_2\text{R}$ is by acylation under Friedel-Crafts conditions followed by reduction of the ferrocenyl ketones.^{11,12,15} Excellent yields of the intermediate ketones are obtained with most acyl chlorides but the preparation by this route of 1,1'-dineopentylferrocene, $\text{R} = \text{CH}_2\cdot\text{CMe}_3$, was unsatisfactory owing to a low yield at the acylation stage. Acylation of ferrocene with 3 mols. of pivaloyl chloride gave a 30% yield of the required 1,1'-dipivaloylferrocene, some monopivaloylferrocene, and a large number of by-products. From the latter, mono-, di-, and tri-*t*-butylferrocenes and 1,1'-dipivaloyl-3,3'-di-*t*-butylferrocene (20%) were isolated. These by-products arise from the decomposition of pivaloyl chloride to carbon monoxide and *t*-butyl chloride with subsequent *t*-butylation of the ferrocene. A reaction similar to that mentioned above has been reported by Pearson¹⁶ who found that *p*-*t*-butylpivalophenone was produced in high yield by treating benzene with pivaloyl chloride in the presence of aluminium chloride. The decomposition of pivaloyl chloride during Friedel-Crafts acylations had been studied by Rothstein and Saville¹⁷ who showed that acylation was dominant if the reactivity of the nucleophilic reagent was high. These authors showed that under similar conditions the amounts of carbon monoxide produced during the reaction between pivaloyl chloride and benzene, pivaloyl chloride and toluene, and pivaloyl chloride and anisole were 87, 53, and 7%, respectively. Under Friedel-Crafts reaction conditions the reactivity of ferrocene would appear to be closely similar to that of anisole, since high yields of monopivaloylferrocene may be obtained. The presence of the first ketonic group then deactivates the remaining unsubstituted cyclopentadiene ring, and the reactivity of this system becomes approximately the same as that of toluene.

An alternative route to 1,1'-dineopentylferrocene is by way of neopentylcyclopentadiene, but because of the inertness of neopentyl halides it was thought unlikely that the above intermediate could be prepared by the direct alkylation of cyclopentadiene. For this reason an indirect route, which made use of the reactive nature of the alkoxy group in unsaturated ethers, was devised. Unsaturated, *e.g.*, allyl and vinyl, ethers are cleaved by Grignard reagents to give the alkylated olefins.¹⁸ It was considered that if they could be obtained, cyclopentadienyl methyl ethers might react in similar manner with *t*-butylmagnesium halides to form neopentylcyclopentadiene. Ethoxymethylcyclopentadiene was

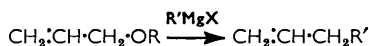
¹⁵ Rosenblum, Whiting, and Woodward, *J. Amer. Chem. Soc.*, 1952, **74**, 3458; Weinmayr, *ibid.*, 1955, **77**, 3009; Graham, Lindsay, Parshall, Peterson, and Whitman, *ibid.*, 1957, **79**, 3416; B.P. 763,550.

¹⁶ Pearson, *J. Amer. Chem. Soc.*, 1950, **72**, 4169.

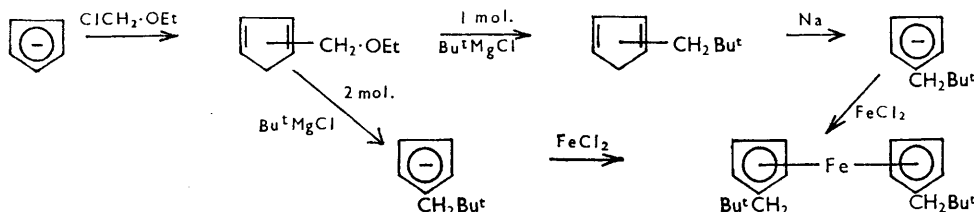
¹⁷ Rothstein and Saville, *J.*, 1949, 1946, 1950, 1954, 1959, 1961; Hsü, Grundy and Rothstein, *J.*, 1952, 4136.

¹⁸ Kharasch and Reinmuth, "Grignard Reactions of Non-metallic Substances," Constable, London, 1954, p. 1015.

prepared from either cyclopentadienylsodium or cyclopentadienylmagnesium bromide and chloromethyl ethyl ether. This ether was more reactive than the corresponding vinyl



and allyl ethers, and by treating it with *t*-butylmagnesium chloride at room temperature neopentylcyclopentadiene was quickly formed in 80% yield. The latter was converted into the sodium derivative, which with ferrous chloride gave 1,1'-dineopentylferrocene. Isolation of the neopentylcyclopentadiene was unnecessary. By using an extra mole of *t*-butylmagnesium chloride the *t*-butyl group was displaced by neopentylcyclopentadienyl to form neopentylcyclopentadienylmagnesium chloride, which with ferrous chloride gave 1,1'-dineopentylferrocene directly. By either of these methods an overall yield of 35% of 1,1'-dineopentylferrocene was obtained from cyclopentadiene.



1,1'-Di-(3,3-dimethylbutyl)ferrocene, the next higher homologue of 1,1'-dineopentylferrocene, was prepared both by the acylation-reduction route and *via* the substituted cyclopentadiene. An attempt to prepare (3,3-dimethylbutyl)cyclopentadiene by treating cyclopentadienylsodium in liquid ammonia with 3,3-dimethylbutyl chloride was unsuccessful, and a relatively high temperature was necessary to accomplish this alkylation.

All the *t*-alkylferrocenes mentioned above were more stable thermally and chemically than the corresponding *n*-alkyl derivatives, and this may be due to the strong electron-release properties of the *t*-alkyl groups. These groups will also sterically hinder the expulsion of the iron atom.

The *t*-alkylferrocenes were prepared during an investigation into the possibility of using ferrocene derivatives for the treatment of iron-deficiency anaemia. When given by mouth to experimental animals, many of these compounds were much better absorbed than the haematinics normally used, and the iron became available for haemoglobin synthesis.

EXPERIMENTAL

Preparation of Reagents.—Finely-dispersed sodium (particle-size 20–100 μ) was prepared by stirring a mixture of sodium (38.0 g.), magnesium stearate (0.5 g.), and sulphur-free toluene (100 c.c.) at 100° with a monel-metal gauze (30 mesh) stirrer (2 in. high \times 1 in. wide) at approximately 5000 r.p.m. for 5 min. The stirrer was stopped and the dispersion was allowed to cool to room temperature. Suspensions of ferrous chloride in tetrahydrofuran were made by adding anhydrous ferric chloride (89.0 g.) to a cooled and stirred mixture of iron powder (20 g.) and tetrahydrofuran (300 c.c.). When all the iron chloride had been added the mixture was gently refluxed in an atmosphere of nitrogen for 3 hr.

t-Butylcyclopentadiene.—The following is a typical preparation of the *t*-alkylcyclopentadienes listed in Table 1. A solution of ethyl bromide in diethyl ether (1000 c.c.) was added to a stirred suspension of magnesium turnings (120 g.) and diethyl ether (800 c.c.) during 2 hr. After stirring for a further hour, cyclopentadiene (264 g.) was added during 30 min. at 20–25° and after stirring for a further 24 hr. *t*-butyl chloride (556 g.) was added during 90 min. The reaction mixture was stirred for 24 hr. and then poured on crushed ice. The ethereal layer was separated, washed with water, and then dried (Na_2SO_4). After removal of ether, the residue was distilled under reduced pressure through a 10 in. Vigreux column and *t*-butylcyclopentadiene, b. p. 45°/28 mm., was collected (320 g., 66%). *t*-Butylcyclopentadiene was stored at 2° for some weeks without any appreciable dimerisation occurring.

1,1'-Di-*t*-butylferrocene from *t*-Butylcyclopentadiene.—For the conversion of *t*-alkylcyclopentadienes into 1,1'-di-*t*-alkylferrocenes the sodium derivatives of the former were prepared

either with finely dispersed sodium in tetrahydrofuran (as described below in the synthesis of 1,1'-di-(3:3-dimethylbutyl)ferrocene or with sodium in liquid ammonia. An example of the latter method is given here. To anhydrous liquid ammonia (2000 c.c.) at -40° in an atmosphere of nitrogen, ferric nitrate crystals (2 g.) and then a small quantity of sodium (5 g.) was added. After reaction began more sodium (87 g.) was added during 1 hr. *t*-Butylcyclopentadiene (530 g.) was added during 30 min. and after 2 hours' stirring tetrahydrofuran (1500 c.c.) was added. The dark brown solution was stirred overnight, the temperature being allowed to rise to 25° and most of the ammonia being driven off. Finally the mixture was refluxed to remove most of the remaining ammonia. The product consisted of a thick but stirrable suspension of large needles of *t*-butylcyclopentadienylsodium. It was cooled to 10° , and a suspension of ferrous chloride in tetrahydrofuran, prepared as described above from ferric chloride (216 g.), was added during 1 hr. After being stirred for 3 hr. the reaction mixture was poured into a mixture of ice and dilute hydrochloric acid. Light petroleum was added and the organic solvent layer was separated and washed free of acid. On evaporation of the petroleum a red oil (475 g.) was obtained which crystallised on stirring with methanol (1000 c.c.) at 3° . The product was filtered and the yellow solid was washed with methanol (500 c.c.) and dried (NaOH) in a desiccator at 5° . The 1,1'-di-*t*-butylferrocene, m. p. $22-24^{\circ}$ (360 g., 61%) was again crystallised from alcohol (1500 c.c.) to give pure material (270 g.), m. p. 28° .

Mono-, 1,1'-Di-, and 1,3-Di-t-butylferrocenes by Alkylation of Ferrocene with t-Butyl Chloride.—Anhydrous aluminium chloride (124 g.) was added during 30 min. to a stirred suspension of ferrocene (144 g.), ethylene dichloride (1500 c.c.), and *t*-butyl chloride (310 c.c.) at 0° . The mixture was stirred at 10° and a slow stream of nitrogen was passed into the apparatus in order to sweep away the hydrochloric acid produced. After 4 hr. the solution was poured on ice. The ethylene dichloride layer was washed with dilute hydrochloric acid, then with dilute sodium hydroxide, and finally with water. Evaporation of this solution at 40° under reduced pressure yielded a red oil (241 g.). The oil was distilled under reduced pressure through a 9 in. \times 1 in. fractionating column packed with stainless-steel gauze rings (efficiency 25 theoretical plates) during 23 hr., and the following fractions were collected.

Fraction	Distillation temp. at 0.2 mm.	Weight (g.)	Main constituent
Fore runnings	33—42°	8.0	—
1	42—63	5.0	—
2	63—71	8.5	<i>t</i> -butylferrocene
3	71—73	14.0	1,3-di- <i>t</i> -butylferrocene
4	78—82	60.0	1,1'-di- <i>t</i> -butylferrocene
5	82—91	15.0	—
6	89—90	12.5	—
7	100—102	5.0	—
8	102—103	31.0	1,1',3-tri- <i>t</i> -butylferrocene
9	103—108	11.5	—
10	108—112	9.5	—
11	112—118	4.0	—
Residue		42.0	1,1',3,3'-tetra- <i>t</i> -butylferrocene
Total		226.0	

By chromatography of fraction 2 on alumina, with light petroleum as solvent, *mono-t-butylferrocene*, m. p. 12° , b. p. $71^{\circ}/0.2$ mm. was obtained. This compound was also prepared in small yield by reaction of a mixture of the sodium derivatives of *t*-butylcyclopentadiene and cyclopentadiene with ferrous chloride (Found: C, 70.5; H, 7.7; Fe, 22.6. $C_{14}H_{18}Fe$ requires C, 69.4; H, 7.4; Fe, 23.2%). Fraction 3 (14.0 g.) quickly crystallised; it was almost pure 1,3-di-*t*-butylferrocene, and was chromatographed on alumina; the first band was 1,1'-di-*t*-butylferrocene and the second contained 1,3-di-*t*-butylferrocene (12.5 g.). After crystallisation from alcohol (100 c.c.), 1,3-di-*t*-butylferrocene was obtained as orange needles, m. p. 63° (Found: C, 72.3; H, 8.5. $C_{18}H_{26}Fe$ requires C, 72.5; H, 8.7%). Fraction 4 was almost pure 1,1'-di-*t*-butylferrocene (60 g., 26% yield from ferrocene) which when crystallised from alcohol (180 c.c.) yielded the pure substance (45 g.), m. p. 28° , identical with that prepared from *t*-butylcyclopentadienylsodium and ferrous chloride. Fractions 7 and 8 (1,1',3-tri-*t*-butylferrocene) crystallised in the condenser during the distillation, and the residue was largely 1,1',3,3'-tetra-*t*-butylferrocene. These derivatives were more conveniently obtained in high yield by the methods described below.

1,1',3-Tri-*t*-butylferrocene.—Anhydrous aluminium chloride (31 g.) was added during 15 min.

to a stirred mixture of ferrocene (36 g.), *t*-butyl chloride (77.5 c.c.), and ethylene dichloride (500 c.c.) at 10°. A stream of nitrogen was passed over the surface of the liquid and the hydrogen chloride produced was absorbed in a solution of sodium hydroxide. The alkylation was allowed to proceed for 6 hr., 2 mols. of hydrogen chloride had then been absorbed by the sodium hydroxide, *i.e.*, 3 mols. actually produced, one being retained in the reaction mixture. The reaction product was treated as described in the foregoing example and after removal of the ethylene dichloride an orange solid resulted (58 g.). This was stirred with alcohol (100 c.c.) at 60°. The mixture was cooled and filtered, and the solid was washed with alcohol to give orange-yellow crystals (51.4 g.), m. p. 79–83°. Chromatographic analysis of a sample of this material showed that it contained *ca.* 5% of 1,1',3,3'-tetra-*t*-butylferrocene. The latter remained behind when the mixture was distilled through a 6 in. Vigreux column. The distillate, b.p. 110°/2 mm., was almost pure 1,1',3-tri-*t*-butylferrocene, m. p. 89–91° (37 g.). A sample crystallised from alcohol had m. p. 91° (Found: C, 74.6; H, 9.3; Fe, 16.6. $C_{22}H_{34}Fe$ requires C, 74.6; H, 9.6; Fe, 15.8%).

1,1',3,3'-Tetra-*t*-butylferrocene.—Like the preceding compounds, 1,1',3,3'-tetra-*t*-butylferrocene was obtained equally readily by alkylation of ferrocene in the presence of either aluminium chloride or zinc chloride. With the latter catalyst a slightly higher temperature was necessary. Powdered zinc chloride (71 g.) was added to a mixture of ferrocene (36 g.), *t*-butyl chloride (150 g.), and ethylene dichloride (200 c.c.). After the mixture had been stirred at 40° for 20 hr. it was poured into dilute hydrochloric acid. A small quantity of zinc dust was added and the mixture stirred until the aqueous layer was nearly colourless. The ethylene dichloride layer was separated and treated as described above. The residue obtained by evaporation of the ethylene dichloride solution was boiled with alcohol (100 c.c.). Filtering the hot mixture and washing the residue with more alcohol yielded 1,1',3,3'-tetra-*t*-butylferrocene (56 g., 68%), m. p. 194–196°. A sample crystallised from alcohol had m. p. 198° (Found: C, 76.2; H, 9.8; Fe, 14.1. $C_{26}H_{42}Fe$ requires C, 76.1; H, 10.2; Fe, 13.7%).

1,1',3,3'-Tetra-*t*-pentylferrocene.—Alkylation of ferrocene with *t*-pentylchloride under conditions similar to those described above yielded 1,1',3,3'-tetra-*t*-pentylferrocene, m. p. 110° (Found: C, 76.7; H, 10.9; Fe, 12.7. $C_{25}H_{40}Fe$ requires C, 77.2; H, 10.7; Fe, 12.1%).

1,1'-Dipivaloylferrocene.—Anhydrous aluminium chloride (293 g., 2.2 mols.) was added during 1 hr. to a stirred mixture of ferrocene, pivaloyl chloride (420 c.c., 3.5 mols.), and ethylene dichloride (3000 c.c.) at 0° in an atmosphere of nitrogen. After being stirred at this temperature for a further 3 hr. the solution was poured on crushed ice, and the organic solvent solution was separated. The latter was washed with water until free from acid. After a further wash with dilute sodium hydroxide, the ethylene dichloride was removed by distillation under reduced pressure. The product was stirred with light petroleum. The insoluble material was filtered and washed with more light petroleum (250 c.c.). Crystallisation of the crude 1,1'-dipivaloylferrocene from alcohol yielded pure material (109 g., 31%), m. p. 127° (Found: C, 67.8; H, 7.3; Fe, 16.4. $C_{20}H_{26}O_2Fe$ requires C, 67.8; H, 7.3; Fe, 15.8%).

Concentration of the petroleum washings yielded a viscous red oil. Chromatography of this oil with alumina and petroleum showed, in addition to a small amount of 1,1'-dipivaloylferrocene and some unchanged ferrocene, *monopivaloylferrocene*, m. p. 92° (Found: C, 66.8; H, 6.5. $C_{18}H_{18}OFe$ requires C, 66.6; H, 6.7%), 1,1'-dipivaloyl-3,3'-di-*t*-butylferrocene, and mono- and di-*t*-butylferrocenes.

1,1'-Dipivaloyl-3,3'-di-*t*-butylferrocene.—By changing the order of addition of the reactants the above tetrasubstituted ferrocene was more readily obtained. To a stirred mixture of powdered anhydrous aluminium chloride (8 g.) and ethylene dichloride (50 c.c.) at 0–5° was added a solution of ferrocene (3.6 g.) and pivaloyl chloride (5.4 g.) in ethylene dichloride (50 c.c.) during 30 min. Stirring was continued at 25° for 1 hr. The solution was poured on ice, and the ethylene dichloride solution was washed and evaporated as described above. Trituration of the residue with light petroleum this time yielded a red insoluble solid (2.9 g.), which crystallised in deep red needles from alcohol (150 c.c.), m. p. 230° (Found: C, 72.0; H, 9.0; Fe, 12.3. $C_{28}H_{42}O_2Fe$ requires C, 72.1; H, 9.0; Fe, 12.0%).

Clemmensen reduction of the above afforded 1,1'-dineopentyl-3,3'-di-*t*-butylferrocene, m. p. 96° (Found: C, 77.5; H, 10.4; Fe, 13.3. $C_{28}H_{46}Fe$ requires: C, 76.8; H, 10.5; Fe, 12.8%).

1,1'-Dineopentylferrocene.—Unlike the preparation of the intermediate, 1,1'-dipivaloylferrocene, Clemmensen reduction of this substance gave a high yield of the dialkylferrocene. Granulated zinc (800 g.) was amalgamated by stirring for 5 min. with a solution of mercuric

chloride (80 g.), water (800 c.c.), and concentrated hydrochloric acid (40 c.c.). The aqueous phase was decanted and alcohol (1600 c.c.), concentrated hydrochloric acid (2200 c.c.), and 1,1'-dipivaloylferrocene (200 g.) were added to the flask. The mixture was stirred vigorously at 95–100° for 6 hr. Whilst hot, the two liquid phases that were formed were decanted from unused zinc; the product quickly crystallised on cooling. The solid yellow cake of 1,1'-dineopentylferrocene was broken up, washed free of acid with water and then stirred with cold methanol (200 c.c.). After filtration and washing with more methanol, orange-yellow crystals (137 g.), m. p. 66–68°, were obtained. Crystallisation from alcohol yielded pure 1,1'-dineopentylferrocene (123 g., 67%), m. p. 69° (Found: C, 73.4; H, 9.0; Fe, 17.5. $C_{20}H_{30}Fe$ requires C, 73.7; H, 9.2; Fe, 17.2%).

Ethoxymethylcyclopentadiene.—Cyclopentadiene (33 g.) was added to a stirred suspension of sodium shot (11.5 g.) in tetrahydrofuran (100 c.c.) at 25–30° in an atmosphere of nitrogen during 30 min. After being stirred for a further 2 hr. the clear solution of cyclopentadienylsodium was transferred to a tap-funnel and added during 30 min. to a stirred solution of chloromethyl ethyl ether (47 g.) and diethyl ether (100 c.c.) at between –5 and 0°. After being stirred for a further 1 hr. at 5–10° the suspension was poured into ice-water. The ethereal solution was separated, washed free of acid, and then dried (Na_2SO_4). The diethyl ether was evaporated at <30° under reduced pressure and the residue was distilled through a 10 in. Vigreux column. *Ethoxymethylcyclopentadiene* was collected, b. p. 22°/1.0 mm. (30 g., 50%) (Found: C, 77.8; H, 9.8. $C_8H_{12}O$ requires C, 77.4; H, 9.7%).

Neopentylcyclopentadiene.—A 2 M-ethereal solution of t-butylmagnesium chloride (150 c.c.) was added to ethoxymethylcyclopentadiene (29 g.) at room temperature, and the flask was immersed in a water-bath to maintain the temperature at 25–30°. After 2 hr. the mixture was poured into ice-water. The ethereal solution was separated, washed with water, and dried (Na_2SO_4). After removal of the ether under reduced pressure, the *neopentylcyclopentadiene* (23 g., 72%) distilled at 38°/7.0 mm. (Found: C, 88.2; H, 11.8. $C_{10}H_{16}$ requires C, 88.3; H, 11.8%). Neopentylcyclopentadiene was also similarly prepared from n-butoxymethylcyclopentadiene.

1,1'-Dineopentylferrocene from Neopentylcyclopentadiene.—A dispersion of sodium (9.0 g.) in toluene (20 c.c.) was prepared as described above and tetrahydrofuran (75 c.c.) was added in an atmosphere of nitrogen. To the stirred mixture, neopentylcyclopentadiene (17.5 g.) was added during 15 min. Slight cooling was necessary to maintain the temperature at 25–30°. Conversion into neopentylcyclopentadienylsodium was complete after a further 2 hr. A suspension of ferrous chloride in tetrahydrofuran, prepared from 7.0 g. of ferric chloride as described above, was added at 10° during 30 min. After being stirred for a further 3 hr. at room temperature the mixture was poured into a mixture of dilute hydrochloric acid and ice. The toluene solution was separated and washed with more dilute hydrochloric acid and then with water. Evaporation under reduced pressure left a red oil (21 g.) which quickly crystallised on cooling. The crystals were washed with alcohol (50 c.c.), and 1,1'-dineopentylferrocene (13.3 g., 63%) was obtained as orange-yellow crystals, after crystallisation from alcohol (30 c.c.), having m. p. 68°, identical with that prepared from 1,1'-dipivaloylferrocene.

1,1'-Di-(3,3-dimethylbutyl)ferrocene via 3,3-dimethylbutylcyclopentadiene.—As stated previously, this was prepared *via* the corresponding di-acylferrocene and also *via* the alkylcyclopentadiene. Owing to the relatively inert nature of 3,3-dimethylbutyl chloride, an attempted alkylation of cyclopentadienylsodium in liquid ammonia was unsuccessful, and the following method was used for the preparation of the required 3,3-dimethylbutylcyclopentadiene.

To a stirred mixture of sodium shot (101 g.) in tetrahydrofuran (1500 c.c.; commercial grade dried over NaOH) at 25–30° in an atmosphere of nitrogen was added cyclopentadiene (281 g.) during 90 min. After being stirred for a further 2 hr. all the sodium had reacted, and 3,3-dimethylbutyl chloride (525 g.) was then added. The resulting solution was gently boiled (internal temp. 74°) for 2 hr. The reaction mixture was cooled and poured into ice-water. The oily layer was separated and washed with water and dried (Na_2SO_4). After being filtered from sodium sulphate the oil was distilled at reduced pressure and 3,3-dimethylbutylcyclopentadiene, b. p. 33–38°/2.0 mm. (221 g., 36%) was collected. Finely-dispersed sodium (38.0 g.) in toluene (100 c.c.) was added to tetrahydrofuran (500 c.c.). 3,3-Dimethylbutylcyclopentadiene (250 g.) was added to the stirred sodium dispersion at 28–35° during 1 hr.; the sodium reacted with a brisk evolution of hydrogen. The mixture was stirred overnight. The suspension of 3,3-dimethylbutylcyclopentadienylsodium was cooled to 10° and a tetrahydrofuran suspension of

ferrous chloride, prepared from ferric chloride (89 g.) as described above, was added during 30 min. After being stirred at room temperature for 4 hr. the mixture was poured into a mixture of dilute hydrochloric acid and ice. Light petroleum (250 c.c.) was added and the organic phase was separated. After a second washing with dilute hydrochloric acid the petroleum solution was washed free from acid and evaporated under reduced pressure to an oil which quickly crystallised on cooling (234 g.). Crystallisation from alcohol (340 c.c.) gave pure 1,1'-*di*-(3,3-dimethylbutyl)ferrocene (167 g., 57%) as yellow plates, m. p. 62° (Found: C, 75.1; H, 9.4. C₂₂H₃₄ requires C, 74.6; H, 9.6%).

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