764. *Ferrocene Derivatives. Part XII.* Di- and Tri-ferrocenylmethane Derivatives.*

By P. L. Pauson and W. E. Watts.

Diferrocenylmethane is obtained from ferrocene and paraformaldehyde. Its conversion *via* diferrocenyl ketone into a series of diferrocenylalkanols is described. αα-Diferrocenylbenzyl alcohol can also be obtained by condensation between ferrocene and benzoylferrocene. Two routes to triferrocenylmethane and to 1,1′-di(ferrocenylmethyl)ferrocene, a new method for preparing ferrocenecarboxyaldehyde, and the aldol condensation of acetylferrocene are reported.

It has been shown by Rinehart *et al.*[1] that the dimeric condensation product obtained from ferrocene and formaldehyde in hydrofluoric[2] or sulphuric acid[3] is 1,2-diferrocenylethane (I; R = H). They showed that ferrocenylmethanol will furnish the same product with acids and interpreted the reaction as proceeding through this alcohol to the carbonium ion (II). The latter was assumed to be in equilibrium with the ferricinium ion radical, $C_5H_5\overset{+}{Fe}C_5H_4{\cdot}CH_2{\cdot}$, which would dimerise to the dication corresponding to the observed product (I; R = H).

$FcCHR{\cdot}CHRFc$	$FcCH_2^+$	Fc_2CHR	Fc_2CO	$Fc_2CR{\cdot}OH$
(I)	(II)	(III)	(IV)	(V)

(Fc = ferrocenyl)

We have now found conditions under which this condensation leads to only small quantities of the latter product and gives mainly diferrocenylmethane (III; R = H). That this compound arises by condensation of the intermediate cation (II) with the excess of ferrocene is confirmed by its alternative preparation from ferrocenylmethanol and ferrocene on treatment with sulphuric acid. The preferred method, however, is the reaction of ferrocene with paraformaldehyde in concentrated sulphuric acid.

The ready availability of diferrocenylmethane by this route makes it a convenient starting material for the preparation of diferrocenyl ketone (IV)[4-6] from which it had previously been obtained by reduction with sodium and ethanol[7] or with lithium aluminium hydride in the presence of aluminium chloride.[6] In the absence of aluminium chloride, the latter reducing agent converts[7] the ketone (IV) into the corresponding alcohol (III; R = OH)[7,8] which we have also obtained (cf. Jutz[9]) by condensation of ferrocenecarboxyaldehyde with ferrocene in presence of aluminium chloride. The alcohol was smoothly converted into the corresponding ether, bisdiferrocenylmethyl ether, on treatment with toluene-*p*-sulphonyl chloride. The related alcohols (V) are also readily accessible from diferrocenyl ketone (IV), as is shown by the preparation of the n-butyl, phenyl, and ferrocenyl derivatives (V; R = Bu^n, Ph, and Fc respectively) by using butyl-, phenyl- and ferrocenyl-lithium. αα-Diferrocenylbenzyl alcohol (V; R = Ph) was smoothly reduced to diferrocenylphenylmethane (III; R = Ph)[10] with zinc and acid, and in a similar fashion triferrocenylmethanol (V; R = Fc) yielded triferrocenylmethane (III;

---

* Part XI, Knox and Pauson, *J.*, 1961, 4615.

[1] Rinehart, Michejda, and Kittle, *J. Amer. Chem. Soc.*, 1959, **81**, 3162.

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

[3] Nesmeyanov and Kritskaya, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1956, 253.

[4] Goldberg, *J. Org. Chem.*, 1960, **25**, 482.

[5] Rausch, Fischer, and Grubert, *J. Amer. Chem. Soc.*, 1960, **82**, 76.

[6] Rinehart, Ellis, Michejda, and Kittle, *J. Amer. Chem. Soc.*, 1960, **82**, 4112; Rinehart, Kittle, and Ellis, *ibid.*, p. 2082.

[7] Schlögl and Mohar, *Monatsh.*, 1961, **92**, 219.

[8] Schaaf, *J. Org. Chem.*, 1962, **27**, 107.

[9] Jutz, *Tetrahedron Letters*, 1959, No. 21, 1.

[10] Weliky and Gould, *J. Amer. Chem. Soc.*, 1957, **79**, 2742.

R = Fc). The latter product was reconverted into the alcohol by hydride abstraction with triphenylmethyl perchlorate, followed by hydrolysis with sodium carbonate solution. The blue oil obtained as an intermediate must contain the triferrocenylmethyl cation and the success of the hydride transfer indicates that the aliphatic C–H bond in triferrocenylmethane is weaker than in triphenylmethane.

Triferrocenylmethane was also obtained as a by-product in low yield by condensation of ferrocene with dichloromethyl ethyl ether in presence of aluminium chloride. The main product of this reaction is the expected [11] aldehyde and this novel route to ferrocenecarboxyaldehyde gives yields comparable to the Vilsmeier reaction.[12–15] It offers advantages in ease of operation and isolation of the product over the latter and alternative methods: [15,16]

$$C_{10}H_{10}Fe + Cl_2CH(OEt) \xrightarrow{AlCl_3} FcCHO + Fc_3CH$$

We were, however, unable to obtain any ferrocene-1,1′-dicarboxyaldehyde [17] by this procedure, even with a large excess of reagents, and attempted formylation of tricarbonylcyclopentadienylmanganese gave only traces of unidentified products.

The availability of αα-diferrocenylbenzyl alcohol (V; R = Ph) by the above method prompted us to compare it with the product to which this structure had previously been tentatively assigned by Weliky and Gould.[10] Their product, said to decompose at 150—170°, was obtained in unspecified yield by treating benzoylferrocene with sodium amalgam in refluxing benzene. Repetition of this procedure gave a 2·3% yield of a product identical in every respect with the above alcohol of m. p. 195—197° (decomp.), together with ferrocene (7·3%) and some benzoic acid. The last two compounds must arise from hydrolysis of the ketone:

$$FcCOPh + NaOH \longrightarrow C_{10}H_{10}Fe + Ph{\cdot}CO_2Na$$

It seemed probable therefore that the alcohol (V; R = Ph) arose by condensation of the ferrocene so formed with benzoylferrocene. Indeed, deliberate addition of ferrocene to the reaction mixture led to the expected increase in yield. Surprisingly, however, even in presence of equimolar amounts of ferrocene the best yields of the alcohol (13—15%) were obtained when the benzene solvent used was deliberately saturated with water, while under anhydrous conditions the benzoylferrocene and ferrocene were recovered quantitatively. Thus water (or the sodium hydroxide derived from it) appears necessary, not only for the hydrolysis of benzoylferrocene, but also for its condensation with ferrocene. This made it appear unlikely that the reaction involved a radical substitution *via* a ketyl intermediate. In conformity with this conclusion the sodium ketyl of benzophenone does not react with ferrocene under analogous conditions.

We consider that the exceptional stability [3,18] of α-ferrocenylcarbonium ions, $FcCR_2^+$, might make possible the addition of sodium ions to benzoylferrocene to give a cation, $FcC^+Ph{\cdot}ONa$, which could condense with ferrocene. However, we were unable to effect condensation between benzoylferrocene and ferrocene when using sodium methoxide as an alternative source of sodium ions. We also failed to effect reaction between ferrocene and the aluminium chloride complex of benzoylferrocene (which we formulate as $FcC^+Ph{\cdot}OAlCl_3^-$), in contrast to the above-mentioned condensation of ferrocenecarboxyaldehyde with ferrocene.

---

[11] Rieche, Gröss, and Höft, *Chem. Ber.*, 1960, **93**, 88.

[12] Rosenblum, *Chem. and Ind.*, 1957, 72.

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

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

[15] Broadhead, Osgerby, and Pauson, *J.*, 1958, 650.

[16] Lindsay and Hauser, *J. Org. Chem.*, 1957, **22**, 355.

[17] Osgerby and Pauson, *J.*, 1961, 4604.

[18] Richards and Hill, *J. Amer. Chem. Soc.*, 1959, **81**, 3484; Hill and Richards, *ibid.*, 1961, **83**, 3840, 4216; Buell, McEwen, and Kleinberg, *Tetrahedron Letters*, 1959, No. 5, 16; Berger, Kleinberg, and McEwen, *Chem. and Ind.*, 1960, **204**, 1245; Arnett and Bushick, *J. Org. Chem.*, 1962, **27**, 111.

Thus the mechanism of Weliky and Gould's reaction[10] remains obscure although our evidence appears to establish the reaction as a condensation between ferrocene and benzoylferrocene. No similar condensation could be effected between ferrocene and benzophenone, acetophenone, or acetylferrocene. The last compound affords the saturated ketone (VII) under these conditions. This must arise by an aldol-type condensation and reduction by the sodium amalgam. We have carried out the condensation reaction separately and isolated the expected unsaturated ketone (VI) and have further reduced both ketones to the saturated alcohol (VIII).

$$\begin{tikzcd}
\mathrm{FcCO{\cdot}CH_3} \arrow[r] & \underset{\text{(VI)}}{\mathrm{FcCMe{:}CH{\cdot}COFc}} \arrow[r] & \underset{\text{(VII)}}{\mathrm{FcCHMe{\cdot}CH_2{\cdot}COFc}} \arrow[d] \\
& \text{(IX) }\mathrm{Fc_2CMe{\cdot}CO{\cdot}CH_3} & \mathrm{FcCHMe{\cdot}CH_2{\cdot}CHFc{\cdot}OH}\text{ (VIII)}
\end{tikzcd}$$

In this connection we have also shown that, like benzoylferrocene,[10] acetylferrocene suffers partial pinacol reduction with zinc and hydrochloric acid and by subsequent pinacol–pinacolone rearrangement yields the ketone (IX) together with ethylferrocene as the normal Clemmensen reduction product.

Finally, we describe here the preparation of the trinuclear 1,1′-di(ferrocenylmethyl)-ferrocene (X). We have previously shown[19] that α-ferrocenylfulvene can be converted into a derivative of this compound (X). We now find that treatment of the fulvene with lithium aluminium hydride affords the intermediate anion (XI) which reacts with ferrous chloride to give the product (X). We had also described[17] an alternative starting material, ferrocenylmethylcyclopentadiene (XII), which was obtained from ferrocenylmethyltrimethylammonium iodide and cyclopentadienylsodium. Repeated attempts to convert this through the same intermediate (XI) into the trinuclear ferrocene (X) failed. We now find that, when the intermediate (XII) is prepared in the presence of an excess of sodium so as to lead directly to the sodium salt of the anion (XI), and ferrous chloride is added immediately to this mixture, a small yield of the same trinuclear ferrocene derivative (X) is obtained.

$(\mathrm{FcCH_2{\cdot}C_5H_4})_2\mathrm{Fe}$ (X) $\qquad \mathrm{FcCH_2{\cdot}C_5H_4^-}$ (XI) $\qquad \mathrm{FcCH_2{\cdot}C_5H_5}$ (XII)

[*Added in proof:* A recent paper by Kenner *et al.* (*J.*, 1962, 1756) draws attention to the formation of triphenylmethanol from benzophenone and potassium hydroxide (Delange, *Bull. Soc. chim. France*, 1903, **29**, 1131; Lock and Rodiger, *Ber.*, 1939, **72**, 861) and describes a related reaction of fluorenone. Both processes appear similar to the reaction of benzoylferrocene[10] discussed above. We have therefore subjected this compound to the conditions employed by Kenner *et al.* This does not lead to formation of the alcohol (V; R = Ph). We have confirmed our previous observation that the addition of ferrocene leads to an increased yield (6—10%) of this alcohol under our conditions, proving that the mechanism suggested by Kenner *et al.* is not applicable to the reaction of benzoylferrocene.]

EXPERIMENTAL

For general remarks see Part X.[20]

Wherever a product was obtained by two routes, identity was established by mixed m. p. and infrared comparison. Molecular weights were determined cryoscopically in benzene.

Diferrocenylmethane.—(*a*) A solution of paraformaldehyde (2·0 g.) in concentrated sulphuric acid (100 ml.) was added to ferrocene (9·3 g.) with stirring at room temperature. An exothermic reaction occurred and the mixture became blue. After 3 hr. the solution was poured into water (200 ml.), and the ferricinium salts present were reduced with an excess of titanous chloride solution. The pale yellow precipitate was filtered off and dissolved in ether, and the

---

[19] Knox, Munro, Pauson, Smith, and Watts, *J.*, 1961, 4619.

[20] Knox and Pauson, *J.*, 1961, 4610.

solution washed with water and dried (Na_2SO_4). The residue after evaporation of the solvent was chromatographed in ligroin on alumina. Ligroin eluted unchanged ferrocene (6·3 g., 66%) followed by diferrocenylmethane (1·8 g.; 58%) which after two recrystallisations from ligroin had m. p. 144—146° (lit.,[7] m. p. 143—149°). Ligroin–benzene (1 : 1) eluted a trace of 1,2-diferrocenylethane, identical with an authentic specimen.[1,3]

(*b*) Concentrated sulphuric acid (100 ml.) was added to an intimate mixture of ferrocene (1·86 g., 10 mmoles) and ferrocenylmethanol (1·08 g., 5 mmole) with vigorous stirring at room temperature. After 3 hr. the mixture was poured into water (200 ml.) and the solution worked up as in the previous experiment. Chromatography of the products gave in order of elution: ferrocene (1·2 g., 64% recovery) eluted by ligroin; diferrocenylmethane (0·56 g., 29%), eluted by ligroin and identical with the compound described under (*a*); di(ferrocenylmethyl) ether (0·18 g., 9%) eluted by benzene, m. p. and mixed m. p. 131—133°; ferrocenylmethanol (0·04 g., 4% recovery) eluted by benzene–ether.

Diferrocenylmethanol.—(*a*) Diferrocenyl ketone [6] (0·40 g., 1 mmole) was dissolved in dry ether (50 ml.), and the solution refluxed for ½ hr. with lithium aluminium hydride (0·40 g., 11 mmoles). The excess of hydride was decomposed with ethyl acetate, the mixture filtered, and the filtrate evaporated. The residue (0·28 g., 70%) was recrystallised twice from cyclohexane to give pure diferrocenylmethanol as rosettes of yellow needles, m. p. 176—177° (lit.,[7,8] m. p. 166—167°, 175—180°) (Found: C, 63·4; H, 5·5. Calc. for $C_{21}H_{20}Fe_2O$: C, 63·0; H, 5·1%).

(*b*) A solution of ferrocene (3·65 g., 0·02 mole) in methylene chloride (25 ml.) was added to a stirred solution of ferrocenecarboxyaldehyde (1·40 g., 0·0065 mole) in methylene chloride (100 ml.) containing aluminium chloride (2·62 g., 0·02 mole). After being stirred for 5 hr. at room temperature the mixture was decomposed with water, and the organic phase separated and combined with several methylene chloride extracts of the aqueous phase. The total extract was washed with water and dried (Na_2SO_4) and the solvent evaporated. The crystalline residue was chromatographed in ligroin–benzene (4 : 1) on alumina. Ligroin eluted ferrocene (3·01 g., 82% recovery), and benzene eluted ferrocenecarboxyaldehyde (0·97 g., 69% recovery). Benzene–ether (1 : 1) eluted diferrocenylmethanol (0·23 g., 58% yield based on unrecovered aldehyde), m. p. 175—177°, identical with the alcohol described under (*a*).

Bis(diferrocenylmethyl) Ether.—Diferrocenylmethanol (0·20 g., 0·5 mmole) was dissolved in benzene (50 ml.) and refluxed for 2 hr. with toluene-*p*-sulphonyl chloride (0·30 g., 1·6 mmoles). The solution was then washed with titanous chloride solution and water, and dried (Na_2SO_4), and the solvent was evaporated. The residue was chromatographed in ligroin–benzene (1 : 1) on alumina. Benzene eluted *bis(diferrocenylmethyl) ether* (0·11 g., 70%) which after recrystallisation from benzene had m. p. 244—245° (decomp.) (Found: C, 64·6; H, 5·0. $C_{42}H_{38}Fe_4O$ requires C, 64·5; H, 4·9%). Benzene–ether (1 : 1) eluted unchanged diferrocenylmethanol (0·04 g., 21% recovery).

αα-Diferrocenylbenzyl Alcohol.—Diferrocenyl ketone (0·20 g., 0·5 mmole) was added to a solution of phenyl-lithium, prepared in ether (100 ml.) from lithium (0·14 g., 0·02 g.-atom) and bromobenzene (0·80 g., 5 mmoles). The mixture was stirred for 2 hr. at room temperature. The excess of lithium and phenyl-lithium was then destroyed with methanol. The mixture was filtered, and the filtrate washed with water, dried (Na_2SO_4), and evaporated. The crystalline yellow residue was chromatographed in benzene on alumina. Only one band developed which, on elution with benzene, yielded *αα-diferrocenylbenzyl alcohol* (0·22 g., 91%). After two recrystallisations from cyclohexane this had m. p. 195—197° (decomp.) with softening from 170° [lit.,[17] m. p. 150—170° (decomp.)] (Found: C, 68·5; H, 5·4. $C_{27}H_{24}Fe_2O$ requires C, 68·1; H, 5·3%).

Diferrocenylphenylmethane.—Zinc dust (0·5 g.) was added to a solution of αα-diferrocenylbenzyl alcohol (0·12 g.) in ethanol (10 ml.) containing a little titanous chloride. The solution was refluxed gently and 0·1N-hydrochloric acid added dropwise during 3 hr. The mixture was then filtered, poured into water, and extracted exhaustively with ether. The extracts were dried (Na_2SO_4) and the solvent was evaporated. The crystalline residue was chromatographed in ligroin on alumina. Only one band developed which, on elution with ligroin–benzene (1 : 1), yielded diferrocenylphenylmethane (0·10 g., 87%) which after two recrystallisations from ligroin had m. p. 133—135° (lit.,[7] m. p. 123—124°) (Found: C, 70·4; H, 5·3. Calc. for $C_{27}H_{24}Fe_2$: C, 70·4; H, 5·3%).

1,1-*Diferrocenylpentan*-1-*ol*.—Diferrocenyl ketone (0·20 g., 0·5 mmole) was added to a solution of n-butyl-lithium in ether prepared at −70° [from lithium (0·14 g., 0·02 g.-atom) and n-butyl bromide (0·69 g., 5 mmoles)] and the mixture stirred and allowed to come to room temperature during 2 hr. A little methanol was added and the mixture filtered. The filtrate was washed with water, dried (Na_2SO_4), and evaporated. The residue was chromatographed in benzene on alumina. Benzene eluted 1,1-*diferrocenylpentan*-1-*ol* (10·20 g., 89%) which after crystallisation from cyclohexane had m. p. 148—150° (Found: C, 66·5; H, 6·6. $C_{25}H_{28}Fe_2O$ requires C, 65·9; H, 6·3%).

Triferrocenylmethanol.—(*a*) Ferrocene (5·58 g., 0·03 mole) was added to ethereal n-butyl-lithium [prepared at −70° from lithium (0·14 g., 0·02 g.-atom) and n-butyl bromide (0·70 g., 5 mmoles)] and the mixture allowed to come to room temperature with stirring during 6 hr. To the solution of ferrocenyl-lithium obtained was added diferrocenyl ketone (0·20 g., 0·5 mmole), and the mixture stirred for a further 2 hr. A little methanol was then added and the mixture filtered. The pale yellow filtrate was washed with water, dried (Na_2SO_4), and evaporated, and the residue chromatographed in ligroin–benzene (4 : 1) on alumina. Ligroin eluted unchanged ferrocene (4·80 g., 86%) and benzene–ligroin (4 : 1) eluted 1,1-diferrocenylpentan-1-ol (0·017 g., 7%), m. p. 148—150° (from benzene–cyclohexane), identical with the compound described in the preceding experiment. Benzene eluted *triferrocenylmethanol* (0·15 g., 53%) which after three recrystallisations from cyclohexane had m. p. 160—162° (Found: C, 63·8, 64·0; H, 5·4, 5·5. $C_{31}H_{28}Fe_3O$ requires C, 63·8; H, 4·9%).

(*b*) To a refluxing solution of triferrocenylmethane (0·59 g.; 1 mmole) in methylene chloride (50 ml.) was added a solution of triphenylmethyl perchlorate (0·50 g., 1·5 mmoles) in methylene chloride (50 ml.). After refluxing for 2 hr. evaporation of the solvent gave a deep blue gum. This was dissolved in aqueous ethanol, and aqueous sodium carbonate was added, giving a red solution, which was extracted exhaustively with ether. The extracts were dried (Na_2SO_4) and evaporated and the residual gum was chromatographed in ligroin on alumina. Benzene eluted triferrocenylmethanol (0·35 g., 57%), identical with the compound described under (*a*).

Triferrocenylmethane.—Zinc dust (0·2 g.) was added to a solution of triferrocenylmethanol (0·05 g.) in ethanol (5 ml.) containing a little titanous chloride. The solution was brought to a gentle reflux and 0·1N-hydrochloric acid added slowly dropwise during 2 hr. The mixture was then poured into water, and the solution extracted exhaustively with ether. The extracts were washed with water, dried (Na_2SO_4), and evaporated, and the residue was chromatographed in benzene on alumina. Benzene eluted *triferrocenylmethane* (0·031 g., 64%), m. p. 303—306°, which was obtained as a powdery yellow solid, m. p. 313—314° after several recrystallisations from benzene or cyclohexane (Found: C, 65·5; H, 5·3%; *M*, 593, 555. $C_{31}H_{28}Fe_3$ requires C, 65·5; H, 5·0%; *M*, 568).

Ferrocenecarboxyaldehyde.—(*a*) A solution of dichloromethyl ethyl ether[21] (3·87 g., 0·03 mole) in methylene chloride (25 ml.) was added dropwise in 15 min. to a stirred mixture of aluminium chloride (5·34 g., 0·04 mole), ferrocene (1·86 g., 0·01 mole) and methylene chloride (100 ml.) at 0°. The mixture was stirred for 7 hr. and left overnight under an inert atmosphere. It was then poured on ice and left for 1 hr. A pale blue precipitate was filtered off, the filtrate was extracted exhaustively with chloroform, the extracts were washed with water and dried (Na_2SO_4), and the solvent was evaporated under reduced pressure. The residual deep red gum was chromatographed in ligroin–benzene (1 : 1) on alumina. Ligroin–benzene (1 : 1) eluted unchanged ferrocene (0·69 g., 37%), and benzene eluted ferrocenecarboxyaldehyde (0·96 g., 72%) which, crystallised from ligroin, had m. p. 120—121° and was identical with an authentic specimen.

(*b*) In an experiment similar to the above, but with 0·5 mole each of dichloromethyl ethyl ether and aluminium chloride and 0·135 mole of ferrocene in only 150 ml. of solvent the blue precipitate referred to was suspended between chloroform and aqueous acetic acid and reduced by addition of zinc dust in portions until the colour had been discharged. The red chloroform layer so obtained was washed with water, dried (Na_2SO_4), and evaporated under reduced pressure. The residual gum, on trituration with benzene, deposited triferrocenylmethane (0·52 g., 2%) identical with the product described above. The yield of aldehyde from this experiment was 57% and the recovery of ferrocene 39%.

Reaction between Benzoylferrocene, Ferrocene, and Sodium Amalgam.—In a typical experiment benzoylferrocene (0·29 g., 1 mmole) and ferrocene (0·19 g., 0·001 mole), dissolved in wet

---

[21] Fischer and Wecker, *Z. physiol. Chem.*, 1942, **272**, 1.

benzene (15 ml.), were refluxed with 5% sodium amalgam (50 g.) for 6 hr. Water was then added, and the organic layer washed with water, dried (Na_2SO_4), and evaporated. The residue was chromatographed in ligroin–benzene (2 : 1) on alumina. Ligroin–benzene (2 : 1) quickly eluted ferrocene (0·252 g., 132%), followed slowly by αα-diferrocenylbenzyl alcohol (0·064 g., 13·4%) identical with the sample described above. Benzene eluted unchanged benzoylferrocene (0·061 g., 21% recovery). The aqueous layer was acidified with dilute hydrochloric acid and extracted with ether. Evaporation of the solvent gave a small amount of benzoic acid.

The annexed Table summarises the results of the various experiments carried out.

Reactants			Products	
Benzoyl-ferrocene (mmole)	Ferrocene (mmole)	Water * (mmole)	αα-Diferrocenyl-benzyl alcohol (%)	Ferrocene (%)
1	—	—	—	—
1	—	Trace	2·3	7·3
1	1	—	—	100
1	1	0·15	7·3	108
1	1	0·30	10·1	122
1	1	0·60 *	13·4	132

* Assuming a content of 0·60 mmole in benzene saturated at 15°.

Analogous reactions between equimolar amounts of ferrocene and benzophenone or acetophenone with sodium amalgam in refluxing water-saturated benzene gave only unchanged ferrocene after working up as described above. Similarly, only starting materials were recovered from reactions between ferrocene, benzoylferrocene, and sodium methoxide in refluxing benzene or methanol. On addition of ferrocene to a solution of benzoylferrocene in methylene chloride containing aluminium chloride and subsequent hydrolysis of the reaction mixture, only starting materials were recovered.

1,3-*Diferrocenylbutan*-1-*one*.—Acetylferrocene (1·14 g., 5 mmoles) was refluxed in water-saturated benzene (15 ml.) for 6 hr. with 7% sodium amalgam (50 g.). The mixture was then filtered and the residual amalgam washed with benzene. The filtrate was evaporated and the residue chromatographed in ligroin–benzene (2 : 1) on alumina. Ligroin–benzene (2 : 1) eluted ferrocene (7 mg.), followed slowly by 1,3-*diferrocenylbutan*-1-*one* (0·61 g., 70%) which crystallised from ligroin in orange needles, m. p. 147—149°, $\nu_{\max.}$ (in CCl_4) 1669 cm.$^{-1}$ (C=O) (Found: C, 65·7; H, 5·75%; *M*, 436. $C_{24}H_{24}Fe_2O$ requires C, 65·5; H, 5·5%; *M*, 440). Ligroin–benzene (1 : 1) eluted unchanged acetylferrocene (0·23 g., 20%).

1,3-*Diferrocenylbut*-2-*en*-1-*one*.—Acetylferrocene (2·28 g., 0·01 mole) was refluxed for 6 hr. in benzene (50 ml.) with potassium t-butoxide (1·12 g., 0·01 mole). The solution was then washed well with water, dried (Na_2SO_4), and concentrated to a deep crimson solution which was chromatographed on alumina. Benzene slowly eluted 1,3-*diferrocenylbut*-2-*en*-1-*one* (1·41 g., 64%) which crystallised from ligroin–benzene in deep red plates, m. p. 118—120°, $\nu_{\max.}$ (in CCl_4) 1650 (C=O) and 1585 cm.$^{-1}$ (C=C) (Found: C, 66·2; H, 5·2. $C_{24}H_{22}Fe_2O$ requires C, 65·8; H, 5·1%).

1,3-*Diferrocenylbutan*-1-*ol*.—(*a*) 1,3-Diferrocenylbut-2-en-1-one (0·44 g., 1 mmole) was dissolved in ethanol (200 ml.) and reduced with sodium (10 g.) until the solution became yellow. The mixture was then poured into water and extracted with benzene. The extracts were washed with water, dried (Na_2SO_4), concentrated to small bulk, and chromatographed. Ligroin–benzene (1 : 2) quickly eluted a pale yellow band which gave a trace of an unidentified yellow gum, followed by 1,3-diferrocenylbutan-1-one (15 mg.), m. p. 146—149°, identical with the ketone described above. Benzene eluted unchanged 1,3-diferrocenylbut-2-en-1-one (0·12 g., 27%), and benzene–ether (10 : 1) eluted 1,3-*diferrocenylbutan*-1-*ol* (0·18 g., 56%) which crystallised from ligroin as a yellow powder, m. p. 109—111°; $\nu_{\max.}$ (in CCl_4) 3571 cm.$^{-1}$ (OH) (Found: C, 65·8; H, 6·2. $C_{24}H_{26}Fe_2O$ requires C, 65·0; H, 5·9%).

(*b*) 1,3-Diferrocenylbutan-1-one (0·11 g., 0·25 mmole) was reduced in ethanol (150 ml.) with sodium as described above. Chromatography of the product on alumina gave starting material (8 mg., 7%) and 1,3-diferrocenylbutan-1-ol (0·081 g., 80%), m. p. 108—110°, identical with the alcohol described above.

Clemmensen Reduction of Acetylferrocene.—Acetylferrocene (2·28 g., 0·01 mole) was dissolved in ethanol (50 ml.), and zinc amalgam (10 g.; prepared by shaking mossy zinc for 5 min. with a solution of 1 g. of mercuric chloride in dilute hydrochloric acid) was added. The mixture was brought to the b. p. and a solution of concentrated hydrochloric acid (5 ml.) in ethanol (10 ml.) added dropwise during 0·5 hr. The mixture was refluxed for a further hour and the solution then decanted from the residual amalgam into water (200 ml.). The solution was extracted with ether, and the ether layer washed, dried (Na_2SO_4), and evaporated. The yellow oil so obtained was chromatographed in benzene on alumina. Benzene quickly eluted ethylferrocene (1·86 g., 87%) followed by 2,2-*diferrocenylbutan*-3-*one* (61 mg., 3%) which sublimed at 180° (bath)/0·02 mm. as a pale yellow powder, m. p. 122—123°, $\nu_{max.}$ (in CCl_4) 1709 cm.$^{-1}$ (C=O) (Found: C, 65·9; H, 5·6. $C_{24}H_{24}Fe_2O$ requires C, 65·5; H, 5·5%).

1,1′-*Di(ferrocenylmethyl)ferrocene.*—(*a*) To α-ferrocenylfulvene (5·24 g., 0·02 mole), dissolved in ether (150 ml.), lithium aluminium hydride (1·85 g., 0·05 mole) was added. After 6 hours' stirring at room temperature a flocculent yellow precipitate had been formed. A slurry of ferrous chloride [from ferric chloride (3·24 g., 0·02 mole)] and tetrahydrofuran (100 ml.) was then added in portions and the mixture stirred for a further 36 hr. The excess of hydride was destroyed with ethyl acetate, and the mixture was poured into water and filtered. The organic phase was separated and dried (Na_2SO_4), and the solvent removed, leaving a red gum which was chromatographed in ligroin on alumina. Ligroin eluted cyclopentadienylmethylferrocene (0·59 g., 11%) which was identified by comparison of its liquid-film infrared spectrum with that of an authentic sample. Benzene eluted 1,1′-*di*(*ferrocenylmethyl*)*ferrocene* (3·1 g., 53%) which crystallised from benzene in powdery nodules, m. p. 166—168° (Found: C, 66·4; H, 5·3%; *M*, 594. $C_{32}H_{30}Fe_3$ requires C, 66·0; H, 5·2%; *M*, 582).

(*b*) Cyclopentadienylsodium was prepared in tetrahydrofuran (150 ml.) from cyclopentadiene (0·66 g., 0·01 mole) and an excess of ultrasonically dispersed sodium (0·69 g., 0·03 g.-atom). When evolution of hydrogen had ceased, (ferrocenylmethyl)trimethylammonium iodide (3·92 g., 0·01 mole) was added and the mixture refluxed for 6 hr. Ferrous chloride [from ferric chloride (1·62 g., 0·01 mole)] was then added. After the mixture had refluxed with stirring for a further 12 hr., a little methanol was added and the solution filtered through kieselguhr. The residue obtained on evaporation of the filtrate was chromatographed in ligroin on alumina. Ligroin eluted cyclopentadienylmethylferrocene (1·1 g., 41%), and benzene eluted 1,1′-di(ferrocenylmethyl)ferrocene (0·35 g., 12%), m. p. 167—169° (from benzene) identical with the sample described under (*a*).

Attempted Reaction between Cyclopentadienylmethylferrocene, Sodium, and Ferrous Chloride.—Freshly distilled cyclopentadienylmethylferrocene (1·32 g., 5 mmoles) was dissolved in tetrahydrofuran (100 ml.), and the solution refluxed with ultrasonically dispersed sodium (0·50 g.; 0·022 g.-atom) for 6 hr. Ferrous chloride [from ferric chloride (1·62 g., 0·01 mole)] was then added and refluxing continued with stirring for a further 15 hr. The mixture was worked up as in the preceding experiment. Chromatography of the product on alumina gave only unchanged cyclopentadienylmethylferrocene (0·98 g., 74%).

This work was supported by the Office of Scientific Research of the Air Research and Development Command, USAF. We thank Mr. T. Boyle for technical assistance and the Ethyl Corporation for supplies of ferrocene.

THE ROYAL COLLEGE OF SCIENCE AND TECHNOLOGY,
GLASGOW, C.1.

[*Received, April* 18*th*, 1962.]