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Ferrocenyl salts as synthons: new ferrocenyl-1,3-diketones

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Abstract

Reaction of (ferrocenylmethyl)trimethylammonium iodide with the mono-sodium salts of a range of acyclic 1,3-diketones leads smoothly to 2-(ferrocenylmethyl)-1,3-diketones $[(C_5H_5)Fe(C_5H_4)CH_2]CH(COR^1)(COR^2)$, but with the corresponding tetrabutylammonium salts deacylation occurs. With the sodium salt of cyclohexane-1,3-dione, disubstitution occurs to give (2,6-dioxocyclohexane-1,1-diyl)bismethyleneferrocene, $[(C_5H_5)Fe(C_5H_4CH_2)]_2C[(CO)_2(CH_2)_3]$. The lithium salt of acetylferrocene reacts with a range of monocarboxylic esters to provide 1-ferrocenyl-1,3-diketones $[(C_5H_5)Fe(C_5H_4)]COCH_2COR$, but simple esters of dicarboxylic acids either do not react, or undergo only monosubstitution.

Keywords: Ferrocene; Diketones; Iron

1. Introduction

The salt (ferrocenylmethyl)trimethylammonium iodide, $[(C_5H_5)Fe(C_5H_4CH_2NMe_3)]^+I^-$ (**1**), has long been known to react with a range of nucleophiles with displacement of volatile trimethylamine [1,2]; on the other hand, the corresponding disubstituted derivative hexa-*N*-methylferrocene-1,1-diylbis(methylammonium iodide), $[Fe(C_5H_4CH_2NMe_3)_2]^{2+}(I^-)_2$ (**2**) has been much less well studied. Thus while the reaction of **1** with triphenylphosphine to yield $[(C_5H_5)Fe(C_5H_4CH_2PPh_3)]^+I^-$ (**3**) is well established [1], the corresponding reaction of **2** to give $[Fe(C_5H_4CH_2PPh_3)_2]^{2+}(I^-)_2$ (**4**) is not, although the preparation of the bromide salt analogous to **4** from $[Fe(C_5H_4CH_2Br)_2]$ and triphenylphosphine has recently been reported [3]. Here we report on the reactions of both **1** and **2** with carbanions, which lead to new types of ferrocenyl 1,3-diketones and ferrocene-substituted carboxylic esters.

We also report the development of Cullen's synthesis of 1-ferrocenyl-1,3-diketones by reaction of lithioacetylferrocene with carboxylic esters [4]. We have previously studied the product formed from ethyl acetate and have shown, by a combination of CP-MAS NMR spectroscopy and X-ray diffraction, that in the solid state this product is solely in the enol form, 1-ferrocenyl-3-hydroxybut-2-en-1-one, but that in solution both keto and enol forms co-exist [5].

2. Results and discussion

Although $[(C_5H_5)Fe(C_5H_4CH_2NMe_3)]^+I^-$ (**1**) reacts very readily with triphenylphosphine to form $[(C_5H_5)Fe(C_5H_4CH_2PPh_3)]^+I^-$ (**3**), the corresponding reaction of $[Fe(C_5H_4CH_2NMe_3)_2]^{2+}(I^-)_2$ (**2**) is extremely sluggish. After overnight refluxing in ethanol, the conditions employed for essentially quantitative conversion of **1** into **3**, a mixture of **2** and triphenylphosphine was virtually unchanged: various reaction conditions, in a range of solvents, were tried, and the most satisfactory was found to be 15 days' refluxing in ethanol to give a 70% yield of **4**, which crystallizes from CH_2Cl_2 as a mono-solvate. In a similar series of investigations, the reactions of **1** with the heavier congeners Ph_3As and Ph_3Sb were studied, but no conditions could be found under which these displaced trimethylamine from **1**; even fusion under dinitrogen of a solid mixture of **1** and Ph_3As failed to effect reaction. Seeking an explanation of the much lower reactiv-

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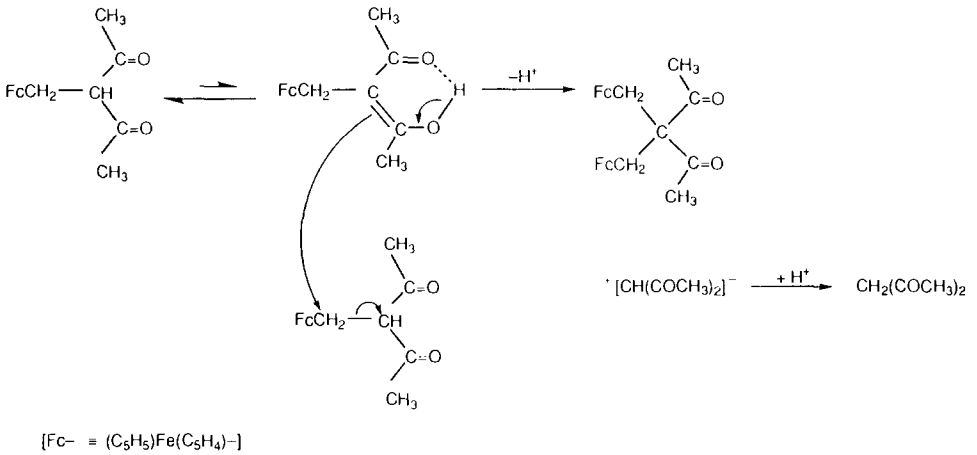
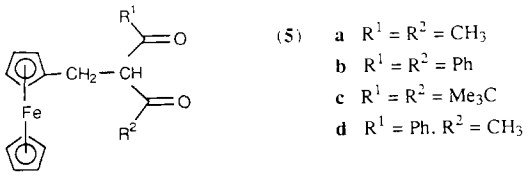


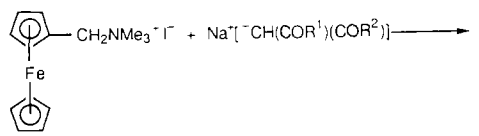
Scheme 1. Possible mechanism for conversion of **5a** into **6**.

ity of **2** than of **1**, we undertook [6] an X-ray structural analysis of both salts; although each salt exhibits in the solid state an extensive network of C–H · · · I^- hydrogen bonds, there are no solid-state features which can be related to the reactivity difference. In solution the only significant difference detectable in the NMR spectra is the observation in **2** but not in **1** of a one-bond $J(^{13}C-^{14}N)$ coupling to the methyl carbons, but not the methylene carbons, identified as such by measurement of the ^{13}C NMR spectrum at three different frequencies. The slow reaction of **2** with Ph_3P, and the complete failure of **1** to react with Ph_3As or Ph_3Sb are so far unexplained.

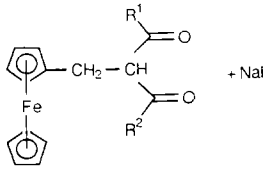
The salt **1** does, however, react very readily with the mono-sodium salts of 1,3-diketones to give the 2-(ferrocenylmethyl)-1,3-diketones **5**, according to Eq. (**1**)



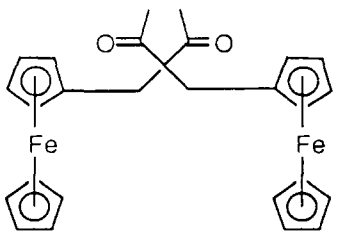
(**5**) **a** $R^1 = R^2 = CH_3$
b $R^1 = R^2 = Ph$
c $R^1 = R^2 = Me_3C$
d $R^1 = Ph$, $R^2 = CH_3$



(1)

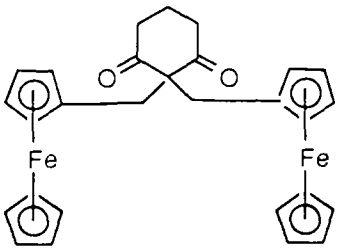


For each of **5a–5d**, the ^1H and ^{13}C NMR spectra in chloroform solution indicated that the keto tautomer predominates; indeed for **5b**, no enol tautomer was detected and only a trace was present in **5d**. For **5a** and **5c** the keto/enol ratios were both ca. 3:1; this is in complete contrast to the situation for 1-ferrocenyl-1,3-diketone $[(C_5H_5)Fe(C_5H_4)]COCH_2COCH_3$ [5], for which the keto/enol ratio in chloroform is 1:17. With the exception of **5a**, all the diketones **5** were obtained as analytically pure, crystalline solids. Compound **5a** on the other hand was obtained as an oil, which upon standing for 6 months deposited crystals analysing as $C_{27}H_{28}Fe_2O_2$ and having remarkably simple NMR spectra; the ^1H spectrum indicated the presence of one acetyl group per ferrocenylmethyl group, and no other hydrogens of any kind; the ^{13}C spectrum indicated one acetyl group per ferrocenylmethyl group, together with a unique quaternary resonance at δ 72.7. These data, and the composition, indicate that the compound has the constitution $[(C_5H_5)Fe(C_5H_4CH_2)]_2C(COCH_3)_2$ (**6**), and is possibly formed as shown in Scheme 1.



(**6**)

A product of similar type was obtained from the reaction between **1** and the monosodium salt of cyclohexane-1,3-dione. Here, no analogue of **5** was observed, but instead **7** was formed showing that double substitution of ferrocenylmethyl groups at the acidic methylene carbon had taken place.

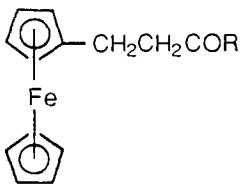


(7)

The formation of compound **7** can be envisaged as occurring via formation of the monosubstituted product, as in Eq. (1), deprotonation by a second mole of 1,3-diketonate anion, and attack by the anion so formed at the exomethylene carbon of a second molecule (Scheme 2).

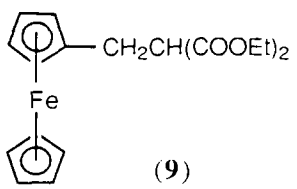
The mass spectra of the diketones **5** all show prominent molecular ions in their mass spectra. In addition all show prominent fragment ions correspond to $(M-78)^+$ and $(M-143)^+$: the strong ion at $m/z = 199$ which is present in all the spectra is assigned as the cation $[(\eta^6-C_6H_6)Fe(\eta^5-C_5H_5)]^+$, isoelectronic with neutral ferrocene. The mass spectrum of the disubstituted product **7** also contained this cation, as well as a strong molecular ion peak.

No tractable products could be obtained from the reactions of compound **1** with the sodium salts of either $CF_3COCH_2COCF_3$ or CH_3COCH_2COOEt, but, clean reactions occurred with both $Na^+[CH(COOEt)_2]^-$ and $Na^+[C(COOEt)_3]^-$, to give in each case ethyl 3-ferrocenylpropanoate (**8a**).

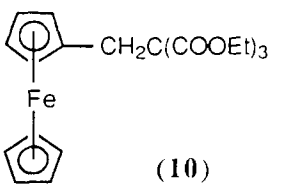


(**8**) **a** R = OEt
b R = CH_3
c R = Ph

In these systems one and two de-esterifications, respectively, occur during the reaction, and despite the exploration of a wide range of reaction times and temperatures with continuous monitoring by TLC, no evidence was obtained for the presence of detectable quantities of either of the expected products **9** and **10**.



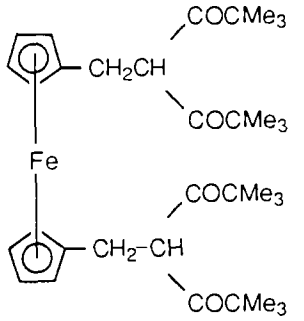
(**9**)



(**10**)

When tetrabutylammonium salts [7] either of pentane-1,3-dione or dibenzoylmethane were treated with (**1**), deacylation was again the dominant reaction, providing respectively **8b** and **8c** as the isolated products.

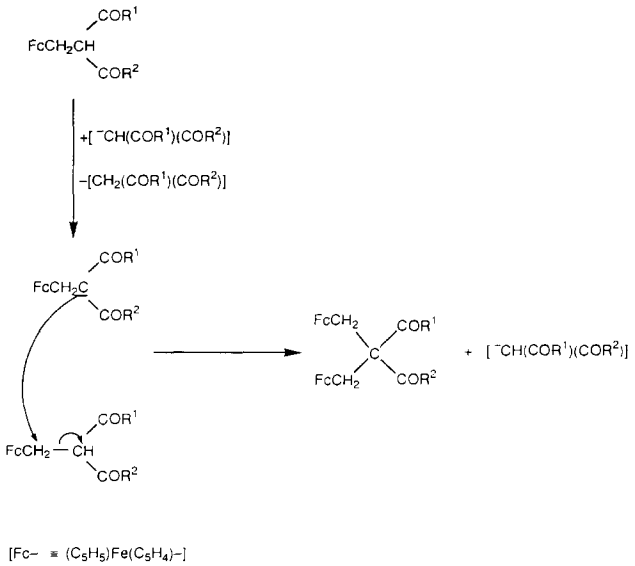
In contrast to the very easy reaction of **1** with the sodium salts of 1,3-diketones, the bis-ammonium salt **2** gave a bis-diketone **11** only with the sodium salt of 2,2,6,6-tetramethylheptane-3,5-dione; no such products were obtained in reactions with the sodium salts of pentane-2,4-dione, dibenzoylmethane, 1-phenylbutane-1,3-dione or cyclohexane-1,3-dione. Compound **11**, however, was obtained analytically pure, and shown by NMR to exist largely in the keto form.



(**11**)

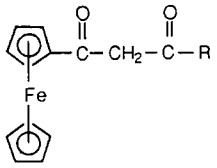
Its mass spectrum contains a strong molecular ion together with prominent fragmentions at m/z 422, 304 and 239, to which we tentatively assign the constitutions $[Fe(Me_3CCOCHCOCMe_3)_2]^+$, $[(C_5H_5)Fe(Me_3COCHCOCMe_3)]^+$, and $[Fe(Me_3CCOCHCOCMe_3)]^+$, respectively.

Concurrently with the development of synthetic routes to ferrocenyl diketones of types **5** and **11**, we developed and extended Cullen's [4] route to the 1-ferrocenyl-1,3-diketones (**12**) (depicted for convenience as the diketo tautomer).



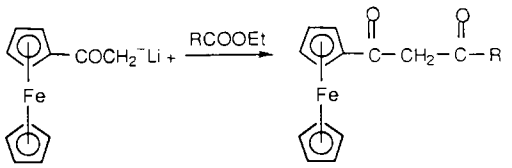
[Fc– = $(C_5H_5)Fe(C_5H_4)$–]

Scheme 2. Proposed mechanism for formation of the doubly-substituted diketone **7**.



(12) **a** R = CH_3
b R = CF_3
c R = Ph
d R = CMe_3
e R = CH_2Ph
f R = $C_6H_4COOMe(p)$

The lithium salt of the acetylferrocene reacts with monoesters to give the diketones **12a–12e**, according to Eq. (2):



For these diketones the keto/enol isomer ratio in chloroform solution ranges from 1:17 for **12a** to 1:5 for **12d** and **12e**; there is thus an interesting contrast between the solution behaviour of the diketones **12** by which the enol form predominates, and that of the diketones **5** and **11**, for which the keto tautomer is the more abundant in solution, and sometimes, as in **5b**, is the sole tautomer detectable. Reflecting this solution behaviour, which points to the more stable tautomer, in the solid state **12a** exists solely [5] as the enol tautomer, whereas **5c** has recently been found [8] to exist in the solid state solely as the diketo tautomer. Although the enol form of **12a** is the more stable in solution by only 7.0 kJ mol^{-1}, and the diketo form of **5c** by only 2.7 kJ mol^{-1}, these differences appear to be sufficient to determine which form is present in the solid state.

Each of **12a–12e** shows a strong molecular ion in the mass spectrum. In addition, the spectrum of **12b** shows a strong ion at $m/z = 702$, i.e. at $[2M + Fe - 2H]^+$, of possible constitution $[Fe\{(C_5H_5)Fe(C_5H_4)COCH\text{-}COCF_3\}_2]^+$, and formed by two molecules, having been deprotonated, chelating an iron from a previously fragmented molecule. Analogous ions were not observed for any other species.

With dimethyl terephthalate, the lithium salt of acetylferrocene yielded only the monosubstitution product **12f**, regardless of the reaction stoichiometry employed; although no pure product could be isolated from corresponding reactions with diethyl phthalate, mass-spectrometric evidence again indicated that only monosubstitution had occurred. By contrast, no tractable products could be isolated from reactions involving simple alkyl esters of maleic, fumaric or succinic acids. In view of the ready reactions with simple esters of representative monocarboxylic acids, the behaviour of diesters is both unexpected and unexplained.

The applications of these new ferrocene-containing 1,3-diketones, both as ligands and as building blocks for macrocycles, will be described in future publications.

3. Experimental details

NMR spectra were recorded at ambient temperature on Bruker AM-300 and MSL-500 spectrometers, for $CDCl_3$ solutions unless otherwise stated. ^{13}C spectra were assigned by use of appropriate DEPT sequences. Sodium salts of 1,3-diketones were made by reaction of the diketone with aqueous sodium hydroxide or with sodium ethoxide.

Compounds **1** and **2** were prepared from ferrocene by aminomethylation followed by methylation [2]. NMR: **1**: δ(H) 3.30 (s, 9H, CH_3); 3.50 (s, 2H, CH_2); 4.35 (s, 5H, C_5H_5); 4.52 (m, 2H) and 4.89 (m, 2H) (C_5H_4); δ(C) 52.8 (q, CH_3); 67.5 (t, CH_2); 69.0 (d), 71.9 (d) and 72.1 (s) (C_5H_4); 70.8 (d, C_5H_5); **2** (CD_3OD solution): δ(H) 3.28 (s, 18H, CH_3), 4.76 (m, 4H) and 4.88 (m, 4H) (C_5H_4), 4.99 (s, 4H, CH_2); δ(C) (CD_3OD), 53.2 (q × t, $^1J(^{13}C\text{–}^{14}N) = 3.8$ Hz, CH_3); 67.5 (t, CH_2); 73.2 (d), 75.1 (d) and 75.9 (s) (C_5H_4). Compound **3** was prepared from **1** by reaction with triphenylphosphine in refluxing ethanol [1]: NMR δ(H) 3.96 (m, 2H) and 4.06 (m, 2H) (C_5H_4); 4.40 (s, 5H, C_5H_5); 5.02 (d, $^2J(HCP) = 10$ Hz, 2H, CH_2); 7.6–7.8 (m, 15H, C_6H_5); δ(C) 28.1 (t × d, $^1J(PC) = 45$ Hz, CH_2); 68.8 (d), 70.1 (d) and 73.6 (s) (C_5H_4); 70.0 (d, C_5H_5); 128.0 (s × d, $^1J(PC) = 85$ Hz), 130.2 (d × d, $J(PC) = 12.3$ Hz), 134.4 (d × d, $J(PC) = 9.8$ Hz) and 135.0 (d × d, $^4J(PC) = 2.1$ Hz) (C_6H_5); δ(P) +19.4.

3.1. Preparation of compound 4

Compound **1** (0.60 g, 1.02 mmol) and triphenylphosphine (0.53 g, 2.04 mmol) were dissolved in dry ethanol (600 cm^3), and the solution was heated under reflux for 15 days then cooled and poured, with vigorous stirring, into dry diethyl ether (75 cm^3). The yellow precipitate was filtered off and recrystallized from CH_2Cl_2 to yield **4** as a CH_2Cl_2 solvate, yellow crystals, m.p. 220°C, (yield 0.70 g, 0.71 mmol, 70%). Anal. Found: C, 55.8; H, 4.2; $C_{48}H_{42}FeI_2P_2CH_2Cl_2$ calc.: C, 54.7; H, 4.1%. NMR δ(H) 3.98 (m, 4H) and 4.45 (m, 4H) (C_5H_4); 5.55 (d, $^2J(HCP) = 13$ Hz, 4H, CH_2); 7.5–7.9 (m, 30H, C_6H_5; δ(C) 25.1 (t × d, $^1J(PC) = 44$ Hz, CH_2); 68.8 (d), 72.2 (d) and 76.1 (s) (C_5H_4); 118.1 (s × d, $^1J(PC) = 85$ Hz), 129.7 (d × d, $J(PC) = 12.6$ Hz), 134.4 (d) and 135.0 (d × d, $J(PC) = 10.0$ Hz) (C_6H_5); δ(P) +19.4. Structure confirmed by X-ray analysis [9].

3.2. Preparation of 2-(ferrocenylmethyl)-1,3-diketones (5)

Typically, equimolar quantities of (ferrocenylmethyl)trimethylammonium iodide (**1**) and the monosodium

salt of the diketone were dissolved in dry acetonitrile, and the solution was heated under reflux for 15 h. The solvent was then removed and the residue dissolved in dry dichloromethane. The solution was filtered if necessary and chromatographed on alumina; elution with dichloromethane yielded the products **5**.

5a: Deep red-brown oil (78% yield). NMR (major isomer) δ(H) 2.11 (s, 6H, 2 × CH_3); 2.90 (d, J = 7 Hz, 2H, CH_2); 3.78 (t, J = 7 Hz, 1H, CH); 4.02 (m, 2H) and 4.06 (m, 2H) (C_5H_4); 4.13 (5H, C_5H_5): δ(C) 29.1 (t, CH_2); 29.8 (q, CH_3); 68.1 (d, $CHCH_2$); 67.8 (d), 68.5 (d) and 70.3 (s) (C_5H_5); 68.7 (s, C_5H_5); 208.0 (CO): (minor isomer) δ(H) 2.20 (s, 6H, 2 × CH_3); 3.37 (s, 2H, CH_2); 4.06 (m, 2H) and 4.10 (m, 2H) (C_5H_4); 4.13 (s, 5H, C_5H_5); 16.7 (s, br, 1H, OHO): δ(C) 23.4 (q, CH_3); 27.6 (t, CH_2); 67.2 (d), 68.4 (d) and 88.0 (s) (C_5H_4); 70.7 (d, C_5H_5); 110.8 (s, $C(CO)_2$); 190.9 (s, CO). Major/minor isomer ratio 3.1. When this oil was kept for 6 months, yellow crystals of **6** were deposited (m.p. 170–172°C, from dichloromethane). Anal. found: C, 66.1; H, 5.9. $C_{27}H_{28}Fe_2O_2$ calc.: C, 65.3; H, 5.6%. NMR: δ(H) 2.03 (s, 6H, 2 × CH_3); 2.92 (s, 4H, 2 × CH_2); 4.10 (m, 4H) and 4.14 (m, 4H) (2 × C_5H_4); 4.15 (s, 10H, 2 × C_5H_5); δ(C) 28.4 (q, CH_3); 32.5 (t, CH_2); 68.1 (d), 69.8 (d) and 82.0 (s) (C_5H_4); 68.9 (d, C_5H_5); 72.7 (s, >C<); 207.0 (s, CO).

5b: Orange crystals (75% yield), m.p. 137–140°C, from acetone. Anal. Found: C, 73.3; H, 5.1. $C_{26}H_{22}FeO_2$ calc.: C, 73.9; H, 5.2%. NMR: δ(H) 3.19 (d, J = 7.2 Hz, 2H, CH_2); 3.98 (m, 2H) and 4.06 (m, 2H) (C_5H_4); 4.10 (s, 5H, C_5H_5); 5.31 (t, J = 7.2 Hz, 1H, CH); 7.3–7.8 (m, 10H, 2 × C_6H_5): δ(C) 30.1 (t, CH_2); 59.7 (d, CH); 67.7 (d), 68.9 (d) and 85.7 (s) (C_5H_4); 68.7 (d, C_5H_5); 127.6 (d), 128.8 (d), 133.4 (d) and 135.9 (s) (C_6H_5); 208.9 (s, CO).

5c: Orange crystals (58% yield), m.p. 153–155°C, from acetone. Anal. Found: C, 69.4; H, 8.0. $C_{22}H_{30}FeO_2$ calc.: C, 69.1; H, 7.9%. NMR: (major isomer) δ(H) 1.10 (s, 18H, 6 × CH_3); 2.85 (d, J = 6.8 Hz, 2H, CH_2); 4.00 (m, 2H) and 4.05 (m, 2H) (C_5H_4); 4.10 (s, 5H, C_5H_5); 4.90 (t, J = 6.8 Hz, 1H, CH); δ(C) 27.0 (q, CH_3); 31.3 (t, CH_2); 44.5 (s, CMe_3); 57.8 (d, $CHCH_2$); 67.6 (d), 68.6 (d) and 85.6 (s) (C_5H_4); 68.6 (d, C_5H_5); 208.9 (s, CO): (minor isomer) δ(H) 1.18 (s, 18H, CH_3); δ(C) 27.3 (q, CH_3); 29.6 (s, CMe_3); 39.3 (t, CH_2); 68.3 (d) and 68.4 (d) (C_5H_4); 68.4 (d, C_5H_5); 90.6 (s, $C(COR)_2$); 201.4 (s, CO). Major/minor isomer ratio 3 : 1.

5d: Orange crystals (77% yield), m.p. 82–84°C, from CH_2Cl_2/light petroleum. Anal. Found: C, 70.4; H, 5.9. $C_{21}H_{20}FeO_2$ calc.: C, 70.0; H, 5.6%. NMR: δ(H) 1.20 (s, 3H, CH_3); 3.10 (d, J = 7.3 Hz, 2H, CH_2); 4.00 (m, 2H) and 4.09 (m, 2H) (C_5H_4); 4.10 (s, 5H, C_5H_5); 4.60 (t, J = 7.3 Hz, 1H, CH); 7.4–8.0 (m, 5H, C_6H_5): δ(C) 28.6 (q, CH_3); 29.6 (t, CH_2); 65.5 (d, $CHCH_2$); 67.7 (d), 68.7 (d) and 85.3 (s) (C_5H_4); 68.6 (d, C_5H_5); 128.7 (d), 128.8 (d), 133.6 (d) and 136.5 (s) (C_6H_5); 195.9 (s) and 203.2 (s) (2 × CO).

3.3. Preparation of (2,6-dioxocyclohexane-1,1-diyl)bismethyleneferrocene (7)

(Ferrocenylmethyl)trimethylammonium iodide (1.93 g, 5.0 mmol) was dissolved in dry acetonitrile (100 cm^3); the sodium salt of cyclohexane-1,3-dione (0.67 g, 5.0 mmol) was added, and the mixture was refluxed for 15 h and then allowed to cool. The solvent was removed and the residue chromatographed on alumina; elution with dichloromethane gave **7** as an orange solid (43% yield), m.p. 210°C (dec.), from dichloromethane. Anal. Found: C, 65.3; H, 5.9. $C_{28}H_{28}Fe_2O_2$ calc.: C, 66.1; H, 5.5%. NMR: δ(H) 1.05 (quintet, J = 6.9 Hz, 2H, CH_2); 1.98 (t, J = 6.9 Hz, 4H, 2 × CH_2); 2.90 (s, 4H, 2 × CH_2); 3.90 (m, 4H) and 4.00 (m, 4H) (2 × C_5H_4); 4.10 (s, 10H, 2 × C_5H_5): δ(C) 15.2 (t, CH_2); 40.2 (t, CH_2); 41.4 (t, CH_2); 68.1 (d), 69.4 (d) and 82.8 (s) (C_5H_4); 68.7 (d, C_5H_5); 71.6 (s, >C<); 213.8 (s, CO).

3.4. Reactions of 1 with $Na^+[CH(COOEt)_2]^-$ and $Na^+[C(COOEt)_3]^-$

Typically, an equimolar mixture of **1** and the sodium salt was kept under dry dinitrogen, for between 1 h and 14 h at a temperature between ambient and 80°C. Work-up as before gave **8a** as the sole product. NMR: δ(H) 1.25 (t, J = 7 Hz, 3H, CH_3); 2.50 (m, 2H) and 2.70 (m, 2H) (2 × CH_2); 4.04 (m, 2H) and 4.07 (m, 2H) (C_5H_4); 4.10 (s, 5H, C_5H_5); 4.13 (q, J = 7 Hz, 2H, OCH_2); δ(C) 14.2 (q, CH_3); 24.9 (t) and 35.7 (t) (2 × CH_2); 60.4 (t, OCH_2); 67.3 (d), 67.9 (d) and 87.5 (s) (C_5H_4); 68.5 (d, C_5H_5); 173.2 (s, CO).

3.5. Reactions of 1 with $Bu_4N^+[CH(COCH_3)_2]^-$ and $Bu_4N^+[CH(COPh)_2]^-$

Reactions were conducted as for sodium salts, but refluxing was for only 2 h. NMR **8b**: δ(C) 28.0 (q, CH_3); 30.1 (t) and 45.2 (t) (2 × CH_2); 68.5 (d), 69.8 (d) and 82.0 (s) (C_5H_4); 68.8 (d, C_5H_5); 206.9 (s, CO). **8c**: δ(H) 2.78 (m, 2H) and 3.20 (m, 2H) (2 × CH_2); 4.10 (m, 2H) and 4.16 (m, 2H) (C_5H_4); 4.15 (s, 5H, C_5H_5); 7.4–8.0 (m, 5H, C_6H_5); δ(C) 24.1 (t) and 40.3 (t) (2 × CH_2); 67.6 (d), 68.4 (d) and 88.3 (s) (C_5H_4); 68.8 (d, C_5H_5); 128.0 (d), 128.6 (d), 133.0 (d) and 136.9 (s) (C_6H_5); 199.5 (s, CO).

3.6. Preparation of 1,1'-bis(4,4-dimethyl-3-oxo-2-pivaloylpentyl)ferrocene (11)

Hexa-*N*-methylferrocene-1,1'diylbis(methylammonium iodide) (**2**) (1.75 g, 3.0 mmol) was dissolved in dry

acetonitrile (100 cm^3) and the sodium salt of 2,2,6,6,-tetramethylheptane-3,5-dione (1.27 g, 6.0 mmol) was added. The mixture was refluxed for 20 h then allowed to cool. The solvent was removed and the residue chromatographed on alumina; elution with CH_2Cl_2 yielded the product **11** as an orange solid (40% yield), m.p. 91–92°C, from ethanol. Anal. Found: C, 70.5; H, 8.6. $C_{34}H_{50}FeO_4$ calc.: C, 70.6; H, 8.7%. NMR (major isomer): δ(H) 1.10 (s, 36H, $12 \times CH_3$); 2.83 (d, $J = 7.5$ Hz, 4H, $2 \times CH_2$); 3.91 (m, 4H) and 3.95 (m, 4H) $2 \times C_5H_4$); 4.48 (t, $J = 7.5$ Hz, 2H, $2 \times$ CH): δ(C) 27.1 (q, CH_3); 31.0 (t, CH_2); 44.5 (s, CMe_3); 58.0 (d, $CH(COR)_2$); 68.6 (d), 69.4 (d) and 86.0 (s) (C_5H_4); 208.9 (s, CO): (minor isomer) δ(H) 1.20 (s, 36H, $12 \times CH_3$); 3.76 (s, 4H, $2 \times CH_2$): δ(C) 27.4 (q, CH_3); 29.6 (t, CH_2); 40.0 (s, CMe_3); 68.5 (d), 69.6 (d) and 86.0 (s) (C_5H_4); 90.7 (s, $-C\equiv$); 203.0 (s, CO). Major/minor isomer ratio 3:1.

3.7. Preparation of 1-ferrocenyl-1,3-diketones (12)

In a typical reaction, lithioacetylferrocene was prepared and used by application of following modifications to Cullen's method [4]: (i) the solvent employed was sodium-dried, deoxygenated THF, rather than hexane; (ii) the lithium salt was not isolated, but instead the appropriate quantity of freshly-distilled ester was injected directly into the THF solution at 0°C; (iii) after extraction of the product diketone, purification was effected by chromatography on alumina or silica columns with dichloromethane or hexane as eluant.

In this manner were prepared the following:

(i) From ethyl acetate, 1-ferrocenylbutane-1,3-dione (**12a**) [4,5].

(ii) From ethyl trifluoroacetate, 1-ferrocenyl-4,4,4-trifluorobutane-1,3-dione (**12b**). Anal. Found: C, 51.8; H, 3.4. $C_{14}H_{11}F_2FeO_2$ calc.: C, 51.9; H, 3.4. NMR: δ(H) (major isomer) 4.24 (s, 5H, C_5H_5); 4.68 (m, 2H) and 4.89 (m, 2H) (C_5H_4); 6.08 (s, 1H, CH); (minor isomer) 4.32 (s, C_5H_5). Major/minor isomer ratio 15:1. δ(C) (major isomer) 69.2 (d), 73.8 (d) and 75.3 (s) (C_5H_4); 70.9 (d, C_5H_5); 93.3 (d, CH); 117.8 (s × q, $^1J(CF) = 281.0$ Hz, CF_3); 171.3 (s × q, $^2J(CF) = 35.6$ Hz, $C(O)CF_3$); 194.6 (s, $C_5H_4C(O)$); (minor isomer) 70.4 (d, C_5H_5).

(iii) From ethyl benzoate, 1-ferrocenyl-3-phenylpropane-1,3-dione (**12c**). NMR: δ(H) (major isomer) 4.16 (s, 5H, C_5H_5); 4.58 (m, 2H) and 4.86 (m, 2H) (C_5H_4); 6.40 (s, 1H, CH); 7.5–7.9 (m, 5H, C_6H_5); 16.6 (s, br, 1H, OHO); (minor isomer) 3.95 (s, 2H, CH_2); 4.10 (s, 5H, C_5H_5); 4.30 (m, 2H) and 4.83 (m, 2H) (C_5H_4). Major/minor isomer ratio 8:1. δ(C) (major isomer) 68.7 (d), 72.3 (d) and 78.2 (s) (C_5H_4); 70.3 (d, C_5H_5); 93.7 (d, CH); 126.7 (d), 128.6 (d), 131.8 (d) and 135.1 (s) (C_6H_5); 179.4 (s) and 194.2 (s) (CO); (minor isomer) 52.2 (t, CH_2); 70.0 (d, C_5H_5); 72.9 (d, C_5H_4); 128.7 (d), 129.0 (d), 133.6 (d) and 137.0 (s) (C_6H_5); 193.3 (s) and 197.3 (s) (CO).

(iv) From ethyl trimethylacetate, 1-ferrocenyl-4,4-dimethylpentane-1,3-dione (**12d**). NMR: δ(H) (major isomer) 1.26 (s, $C(CH_3)_3$); 4.17 (s, 5H, C_5H_5); 4.47 (m, 2H) and 4.80 (m, 2H) (C_5H_4); 5.84 (s, 1H, CH); 16.2 (s, br, 1H, OHO); (minor isomer) 1.26 (s, $C(CH_3)_3$); 3.92 (s, 2H, CH_2); 4.30 (s, 5H, C_5H_5); 4.53 (m, 2H) and 4.76 (m, 2H) (C_5H_4). Major/minor isomer ratio 5:1. δ(C) (major isomer). 27.6 (q, CH_3); 38.3 (s, CMe_3); 68.6 (d), 71.9 (d) and 78.3 (s) (C_5H_4); 70.2 (d, C_5H_5); 92.4 (d, CH); 193.3 (s) and 195.8 (s) (CO); (minor isomer) 26.2 (q, CH_3); 48.6 (t, CH_2); 69.7 (d) and 72.7 (d) (C_5H_4); 69.9 (d, C_5H_5).

(v) From ethyl phenylacetate, 1-ferrocenyl-4-phenylbutane-1,3-dione (**12e**). NMR: δ(H) (major isomer) 36.5 (s, 2H, CH_2Ph); 4.16 (s, 5H, C_5H_5); 4.50 (m, 2H) and 4.72 (m, 2H) (C_5H_4); 5.65 (s, 1H, CH); 7.2–7.5 (m, C_6H_5); (minor isomer) 3.82 (s, 2H) and 3.92 (s, 2H) ($2 \times CH_2$); 4.20 (s, 5H, C_5H_5); 4.58 (m, 2H) and 4.76 (m, 2H) (C_5H_4); 7.2–7.5 (m, C_6H_5). Major/minor isomer ratio 5:1. δ(C) (major isomer): 44.3 (t, CH_2); 68.6 (d), 72.1 (d) and 79.0 (s) (C_5H_4); 70.3 (d, C_5H_5); 96.9 (d, $CH(COR)_2$); 127.0 (d), 128.7 (d), 129.3 (d) and 135.8 (s) (C_6H_5); 187.5 (s) and 192.6 ($2 \times CO$); (minor isomer) 50.5 (t) and 53.5 (t) ($2 \times CH_2$); 69.8 (d), 73.0 (d) and 82.0 (s) (C_5H_4); 70.0, C_5H_5); 127.2 (d), 128.8 (d), 129.7 (d) and 134.0 (s) C_6H_5); 197.5 (s) and 202.0 (s) ($2 \times CO$).

(vi) From dimethyl terephthalate, 1-ferrocenyl-3-(4-carbomethoxyphenyl)-propane-1,3-dione (**12f**). NMR: δ(H) (major isomer) 3.95 (s, 3H, CH_3); 4.24 (s, 5H, C_5H_5); 4.63 (m, 2H) and 4.94 (m, 2H) (C_5H_4); 6.40 (s, 1H, $HC(COR)_2$); 8.0–8.2 (m, 4H, C_6h_4); 16.4 (s, br, 1H, OHO); (minor isomer) 4.24 (s, 5H, C_5H_5); 4.37 (m, 2H) and 5.30 (m, 2H) (C_5H_4). δ(C) (major isomer) 52.4 (q, CH_3); 68.9 (d), 72.6 (d) and 78.1 (s, C_5H_4); 70.4 (d, C_5H_5); 94.7 (d, $HC(COR)_2$); 126.6 (d), 129.8 (d), 132.7 (s) and 139.1 (s) (C_6H_4); 166.4 (s), 177.2 (s) and 195.2 (s) ($3 \times CO$); (minor isomer) 53.4 (q, CH_3); 65.2 (t, CH_2); 69.8 (d) and 69.9 (d) (C_5H_4); 70.1 (d, C_5H_5); 126.9 (d), 129.5 (d) and 133.9 (s) (C_6H_4) 166.3 (s, CO).

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