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# THE REACTION OF SOME FERROCENYL KETONES WITH ANHYDROUS SILVER TETRAFLUOROBORATE, A NEW ROUTE TO SUBSTITUTED FERRICENIUM SALTS

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## SUMMARY

Several mono- and diacylferrocenes have been oxidized to the corresponding ferricenium cations by anhydrous silver tetrafluoroborate in non-aqueous media. Monoacylferricenium salts and reduced silver metal are instantly precipitated from ethereal solutions; extraction with liquid sulphur dioxide affords stable, crystalline salts. Disubstituted ferrocenyl ketones are not directly oxidized by silver tetrafluoroborate in diethyl ether to the ferricenium species but form insoluble red 1/1 complexes. These silver complexes of the diacetylferrocenes all show evidence of bonding to silver through the carbonyl groups. Exposure of the 1,1'- and 1,3-diacetylferrocene complexes to liquid sulphur dioxide affords the corresponding 1,1'- and 1,3-diacetylferricenium species; the 1,2-diacetylferrocene complex however reacts in a different way.

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## INTRODUCTION

One of the simplest and most characteristic reactions of the metallocenes is their oxidation to cationic species involving loss of one or more electrons. Ferrocene can be oxidized to the ferricenium cation electrolytically, photolytically and by a wide variety of organic and inorganic oxidizing agents[1].

Little is known of the chemical and physical properties of substituted ferricenium compounds although the effect of substituents on the redox potentials has been investigated. Ferricenium salts are moderately stable in aqueous acid solution but they rapidly decompose in many organic solvents[2]. It is difficult to prepare substituted ferricenium cations because of their instability towards water. So we have studied the preparation of substituted ferricenium cations by the reactions of anhydrous silver tetrafluoroborate with several mono- and disubstituted ferrocenyl ketones in non-aqueous media.

## RESULTS AND DISCUSSION

The preparation of starting materials, isolation of the complexes and their subsequent conversion to substituted ferricenium derivatives is described in the experimental section.

Anhydrous silver tetrafluoroborate readily forms complexes with electron donor molecules both with $\pi$-donors and electron pair donors[3]. The stability of these silver salts in solvents such as diethyl ether and benzene together with the fact that aqueous silver sulphate[4] had been used to oxidize ferrocene to ferricenium, suggested to us that non-aqueous solutions of silver tetrafluoroborate would probably oxidize ferrocene and substituted ferrocene derivatives to the corresponding ferricenium and substituted ferricenium cations. We have prepared several new acylferricenium salts by this method.

$$\mathrm{FcCOR + AgBF_4 \xrightarrow{Ether} (FcCOR)^+BF_4^- + Ag}$$

$$\mathrm{Fc = ferrocenyl = C_5H_5FeC_5H_4-}$$

The monoacylferricenium compounds in Table 1 were prepared by adding a dry, ethereal solution of the ferrocenyl ketone to a solution of the silver salt also in anhydrous ether. The colour of the ferrocene compound was instantly discharged and a black precipitate formed. Filtration of the solid under nitrogen and extraction with dry liquid sulphur dioxide gave crystalline solids, which were moisture sensitive, in almost quantitative yield.

TABLE 1

ANALYTICAL RESULTS AND MAGNETIC DATA FOR ACYLFERRICENIUM TETRAFLUOROBORATES

| Acyl group | Required(%) | | Found(%) | | $\mu_{eff}$ (BM) at 20° |
|---|---|---|---|---|---|
| | C | H | C | H | |
| Acetyl | 45.77 | 3.84 | 45.53 | 3.83 | 2.54 |
| Benzoyl | 54.16 | 3.74 | 54.24 | 3.85 | 2.25 |
| 1,1'-(1-Oxotrimethylene) | 47.76 | 3.70 | 47.63 | 3.66 | 2.28 |
| 1,2-(1-Oxotetramethylene) | 49.32 | 4.14 | 48.92 | 4.01 | 2.32 |

The infrared spectrum of the ferricenium cation has been studied by several workers[4–6]. Pavlik has carried out complete vibrational analyses on several ferricenium salts; he concluded that the considerable shifts in the positions of C–C, C–H and ring–metal vibrations which occur on oxidation indicate that bonding conditions change in the following way:

(*i*). The ring to metal bonds in ferricenium salts are weaker than in ferrocenes;

(*ii*). The C–C bonds in the cyclopentadienyl rings are stronger in ferricenium owing to a decreased participation of $\pi$-electrons in bonding the rings to the central metal atom.

We have similarly attempted to correlate shifts in the infrared spectra of the acylferricenium species with changes in the bonding conditions after oxidation. The infrared spectra of the neutral and oxidized derivatives are very complex and only the vibrations which could be reliably assigned have been selected[7,8].

The most intense and easily assigned bands in the infrared spectra are those due to the acyl group and to vibrations of the ring to metal bonds. The former occur in the region 1620–1700 $\mathrm{cm^{-1}}$ and can be assigned to a stretching mode $\nu$(C=O) of the carbonyl groups; some of the strong bands in the 380–490 $\mathrm{cm^{-1}}$ region are attributable

TABLE 2

COMPARISON OF THE INFRARED SPECTRA[a] OF ACYLFERRICENIUM TETRAFLUOROBORATES ($cm^{-1}$)

| Acyl group | Neutral form | | Oxidised form | | $\Delta\nu(C{=}O)$ | $\Delta\nu_a(Fe{-}C)$ |
|---|---|---|---|---|---|---|
| | $\nu(C{=}O)$ | $\nu_a(Fe{-}C)^b$ | $\nu(C{=}O)$ | $\nu_a(Fe{-}C)^b$ | | |
| Benzoyl | 1621 | 484 | 1655 | 383 | +34 | −101 |
| Acetyl | 1656 | 483 | 1690 | 419 | +34 | − 64 |
| 1,1′-(1-Oxotrimethylene) | 1658 | 491 | 1694 | 373 | +36 | −118 |
| 1,2-(Oxotetramethylene) | 1667 | 499 | 1697 | 403 | +30 | − 96 |

[a] In Nujol mulls. [b] Antisymmetric iron–carbon stretching frequency.

to an antisymmetric ring–metal stretching frequency $\nu_a$(Fe–C). The symmetric ring–metal stretch is inactive or, at best, very weak in the infrared.

The frequencies $\nu$(C=O) of the acylferricenium ions are all shifted by 30–40 $cm^{-1}$ to higher wave numbers when compared with the neutral molecules indicating an apparent strengthening of the carbonyl bond in the oxidized form. The antisymmetric ring–metal frequencies are all shifted to lower wave-numbers by between 60–120 $cm^{-1}$. These shifts are complementary to one another. A weakening of the ring to metal bonds increases the electron density on the cyclopentadienyl rings which in turn leads to stronger bonding conditions within the ligand moiety. The decreased strength of the ring–metal bonds is also manifest as a greatly decreased stability of these ferricenium cations compared with the neutral compounds.

The silver(I) cation can either act as an oxidizing agent or as a Lewis acid depending on the nature of the compounds it is interacting with. It has been shown that silver(I) will oxidize several monoacylferrocenes, depositing silver metal from ether solution. However, not all the ferrocenyl ketones that were prepared could be smoothly oxidized in this manner. 1,1′-, 1,2- And 1,3-diacetylferrocenes were not directly oxidized to the ferricenium derivatives but formed red complexes with silver tetrafluoroborate. These complexes have a 1/1 stoichiometry and their infrared spectra show bonding to the silver ion through both oxygen atoms of the carbonyl groups.

There are two conceivable structure types for these complexes: monomeric or oligo-(even poly-)meric. Unfortunately it was not possible to determine the molecular weights of these compounds because they are insoluble in all common solvents and

TABLE 3

ANALYTICAL RESULTS AND INFRARED DATA FOR DIACETYLFERROCENE SILVER TETRAFLUOROBORATE COMPLEXES

| Complex | Required (%) | | | Found (%) | | | $\Delta\nu(C{=}O)^a$ ($cm^{-1}$) |
|---|---|---|---|---|---|---|---|
| | C | H | Ag | C | H | Ag | |
| 1,1′-DAF·$AgBF_4$ | 36.11 | 3.04 | 23.22 | 36.00 | 3.43 | 23.04 | −49 |
| 1,2-DAF·$AgBF_4$ | 36.11 | 3.04 | 23.22 | 36.37 | 3.16 | 23.01 | −50 |
| 1,3-DAF·$AgBF_4$ | 36.11 | 3.04 | 23.22 | 35.83 | 3.35 | 23.10 | −46 |

[a] Free ketone → adduct.

are also involatile. The insoluble nature of all three adducts is indicative of a polymeric structure. Moreover, the steric restrictions for the adducts of 1,2- and 1,3-diacetylferrocene make monomeric structures highly improbable.

An attempt was made to obtain the $^1$H NMR spectrum of the 1,1'-diacetylferrocene complex in liquid sulphur dioxide. A sample of the complex and dry sulphur dioxide were sealed off in vacuo in an NMR tube. On warming up to room temperature the solution became blue and a grey precipitate was formed. This experiment was repeated on a larger scale and the complex allowed to remain in contact with the sulphur dioxide just below its boiling point for two hours. Filtration of the solution and removal of the solvent gave dark blue crystals of pure 1,1'-diacetylferricenium tetrafluoroborate. The other silver complexes were found to be oxidized in a similar fashion when they were allowed to interact with liquid sulphur dioxide at just below its boiling point.

Unlike the 1,1'- and 1,3- isomers the 1,2-diacetylferrocene complex did not give the blue ferricenium salt on exposure to sulphur dioxide; instead a brown solid, which was extremely sensitive to moisture, was produced. The colour, diamagnetism, $^1$H NMR and infrared spectra of the brown fluoroborate species indicated that it was not a ferricenium salt. The $^1$H NMR spectrum in liquid sulphur dioxide resembles that of 1,2-diacetylferrocene itself and in the infrared, the strong carbonyl stretching frequency is moved by about 70 cm$^{-1}$ to lower wave-numbers. On the other hand the carbonyl stretches in the 1,1'- and 1,3-diacetylferricenium cations have shifted to higher wave-numbers (about 30 cm$^{-1}$). The exact nature of this tetrafluoroborate salt derived from the 1,2-diacetylferrocene complex is not known. It may be a carbonium ion derived from 1,2-diacetylferrocene. It was noted that the silver metal was deposited gradually, as a silver mirror, when the silver fluoroborate complex was allowed to interact with liquid sulphur dioxide.

TABLE 4

ANALYTICAL RESULTS AND INFRARED DATA FOR DIACETYLFERRICENIUM TETRAFLUOROBORATES

| Position of acetyls | Required (%) | | Found (%) | | $\Delta\nu$(C=O)$^a$ (cm$^{-1}$) |
|---|---|---|---|---|---|
| | C | H | C | H | |
| 1,1'- | 47.11 | 3.95 | 47.23 | 3.95 | +30 |
| 1,2- | 47.11 | 3.95 | 47.03 | 4.11 | −69 |
| 1,3- | 47.11 | 3.95 | 46.67 | 3.97 | +34 |

[a] Free ketone → oxidized ketone.

1,1'-Dibenzoylferrocene and silver tetrafluoroborate did not appear to react, either by complex formation or by redox reaction to the ferricenium species. Since oxidation involves the removal of electrons from the neutral compound, the relative ease of oxidation depends on the nature of the substituents. Benzoyl groups are strongly electron withdrawing and the presence of one of these groups on each of the cyclopentadienyl rings in ferrocene makes it much less susceptible to oxidation than other substituted ferrocenes. It was also found that (monoacetylcyclopentadienyl)-manganese tricarbonyl did not react with silver tetrafluoroborate. The weaker basic properties of this compound are reflected in its solubilities in concentrated acids, it is only slightly soluble in concentrated hydrochloric acid whereas monoacetylferrocene is appreciably soluble giving an intensely coloured solution.

## EXPERIMENTAL

All melting points were determined using a Kofler hot stage and are uncorrected. Infrared spectra were recorded on either a Perkin–Elmer 521 or 125 spectrophotometer; ultraviolet and visible spectra on a Unicam SP 800 and $^1$H NMR spectra on a Perkin–Elmer R 10 instrument. Analyses were performed by Alfred Bernhardt, Mülheim, Germany and at the Microanalytical Laboratories of the Chemistry Department, University of Strathclyde.

Manipulations of anhydrous silver tetrafluoroborate, the ferricenium salts and the complexes was carried out in a dry nitrogen atmosphere glove-box, dew-point less than −30°. All solvents were purified and dried by standard methods.

Monoacetylferrocene, 1,2-diacetylferrocene and 1,1′-diacetylferrocene were obtained by acetylation of ferrocene in the usual Friedel-Crafts manner using either aluminium trichloride/acetylchloride or boron trifluoride/acetic anhydride mixtures[9].

Monobenzoylferrocene and 1,1′-dibenzoylferrocene were prepared by a Friedel–Crafts reaction of benzoyl chloride/aluminium trichloride with ferrocene[10].

1,2-(1-Oxotetramethylene)- and 1,1′-(1-oxotrimethylene)ferrocenes were prepared by cyclization of $\omega$-ferrocenylcarboxylic acids with trifluoroacetic anhydride according to the method of Rinehart[11].

### *Preparation of* 1,3-*diacetylferrocene*

This was obtained by oxidation of 1-acetyl-3-ethylferrocene using "active" manganese dioxide. Monoacetylation of ethylferrocene yields a mixture of three isomeric acetylethylferrocenes[13]. 1-Acetyl-3-ethylferrocene was separated from the other isomers by very careful chromatography on alumina. Its purity was checked by comparing its infrared spectrum with that published[13]. A 50/50 mixture of ether/petroleum ether (b.p. 40–60°) eluted the ferrocene derivatives in the following sequence: unchanged ethylferrocene, 1-acetyl-2-ethylferrocene and a mixture of 1-acetyl-1′-ethyl- and 1-acetyl-3-ethylferrocenes. These last two isomers could not be clearly separated into two bands and fractions were taken from the column every 100 ml, the solvent removed and the composition of the fraction checked by infrared spectroscopy. 1-Acetyl-3-ethylferrocene possesses an unsubstituted cyclopentadienyl ring and hence has bands near 1000 and 1100 cm$^{-1}$; thus it could be distinguished from the 1,1′-isomer which precedes it off the column (there are other small but distinct differences in the infrared spectra of the 1,1′- and 1,3-isomers).

Manganese(II) nitrate (1 litre of a 50% solution), 72% perchloric acid (34 ml) and distilled water (1500 ml) were stirred at room temperature for 18 h, during which time an ozone/oxygen mixture was bubbled through the solution (flow rate of 30 l/h)[12]. The precipitated "active" manganese dioxide was filtered off, washed well with distilled water and dried overnight in an oven at 150°. Yield 50 g.

To a solution of 1-acetyl-3-ethylferrocene (9.74 g, 0.04 mole) in dry benzene (150 ml) was added active manganese dioxide (50 g) and the resulting suspension was stirred and refluxed under dry nitrogen, the reaction being followed by TLC. Unchanged starting material moved rapidly up the plate when eluting with a 50/50 mixture of ether/petroleum ether (b.p. 40–60°) leaving 1,3-diacetylferrocene as a separate orange spot. After 48 h the intensity of the colour of the spot due to the diketone did not increase further and the heating was stopped. After cooling to room temperature the solution was filtered and the benzene removed under reduced pressure leaving an orange oil. This was taken up in a few ml of methylene chloride and chromatographed on alumina. Unreacted 1-acetyl-3-ethylferrocene (8 g, 0.031 mole) was rapidly eluted off the column with 50/50 ether/petroleum ether. A second component which developed as an orange band was eluted with 80/20 ether/petroleum ether and was found to be 1,3-diacetylferrocene (0.70 g, 0.003 mole, 38% based on reacted 1-acetyl-3-ethylferrocene). Crystallisation from hot petroleum ether (b.p. 100–120°) afforded orange crystals, m.p. 180–181°. (Found: C, 62.62; H, 5.58. $C_{14}H_{14}FeO_2$ calcd.: C, 62.23; H, 5.22%.)

The $^1$H NMR spectrum in deuterochloroform consisted of a singlet $\tau$ 7.56 (6 H) the methyl group protons, another singlet at $\tau$ 5.72 (5 H) the five protons on the unsubstituted ring, a doublet at $\tau$ 4.94 (2 H) the two protons on the substituted ring adjacent to one another and a triplet at $\tau$ 4.60 (1 H) the isolated proton on the substituted ring.

The ultraviolet/visible spectrum in absolute ethanol had the following absorption maxima at 232, 259, 345 and 450 m$\mu$ ($\varepsilon$ 16240, 10450, 6293 and 4422 respectively).

The infrared spectrum (as a KBr pellet) had strong bands at 1656 cm$^{-1}$, C–O stretching of the carbonyl groups, 1105 and 1005 cm$^{-1}$, an unsubstituted cyclopentadienyl ring, and other bands at 1460 s, 1410 m, 1365 s, 1328 m, 1305 m, 1235 vs, 1198 m, 1073 m, 969 m, 905 w, 892 s, 850 m, 832 s, 565 w, 545 s, 512 s, 498 s, 485 m and 450 w.

1,3-Diacetylferrocene has very similar physical properties to the 1,1'-isomer although the latter is much darker in colour. They cannot be separated by TLC on alumina or silica, are slightly soluble in petroleum ether, moderately soluble in ether and benzene and very soluble in chloroform, methylene chloride and concentrated acids.

### *Preparation of acylferricenium salts*

The preparation of monoacetylferricenium tetrafluoroborate is described as a typical example. Anhydrous silver tetrafluoroborate (0.32 g, 0.0016 mole) was dissolved with stirring in dry ether (100 ml) under nitrogen at room temperature. A solution of monoacetylferrocene (0.39 g, 0.0017 mole) in dry ether was added dropwise to the silver solution. On mixing the solutions there was immediate precipitation of a grey/black solid. This was filtered off under nitrogen, washed several times with dry ether (5×25 ml portions) and pumped to $10^{-4}$ mm. Dry liquid sulphur dioxide (20 ml distilled from $P_2O_5$) was added to the solid giving an immediate blue colour typical of the ferricenium cation. This solution was filtered under nitrogen into a small Schlenk tube and the solvent removed in a steady stream of dry nitrogen. Pumping the solid at $10^{-4}$ mm for several hours removed the last traces of sulphur dioxide leaving a dark blue crystalline solid.

Elemental analyses and magnetic data for the acylferricenium compounds prepared are listed in Table 1.

*Preparation of* 1/1 *complexes of the diacetylferrocenes and silver tetrafluoroborate*

These complexes were prepared by reacting stoichiometric amounts of silver tetrafluoroborate and the ferrocenyl ketone in anhydrous ether. The preparation of 1,1'-diacetylferrocene silver tetrafluoroborate is described.

1,1'-Diacetylferrocene (0.50 g, 0.0019 mole) was dissolved in dry ether (150 ml) under nitrogen at room temperature. Silver fluoroborate (0.34 g, 0.0017 mole) was dissolved in an equal volume of dry ether and was added dropwise to the stirred solution of the ferrocenyl ketone. There was immediate precipitation of a red solid which was filtered off under nitrogen, washed with dry ether (5 × 25 ml portions) and pumped to dryness at $10^{-4}$ mm. Elemental analyses indicated a 1/1 stoichiometry (Table 3).

1,2-Diacetylferrocene formed a similar red compound with silver tetrafluoroborate but if excess silver fluoroborate was used the red complex was formed but almost immediately decomposed to a brown solid which contained no silver and was soluble in liquid sulphur dioxide.

*Preparation of* 1,1'-*diacetylferricenium and* 1,3-*diacetylferricenium salts*

Dry liquid sulphur dioxide (50 ml) was condensed onto the red complex *e.g.* 1,3-diacetylferrocene/silver fluoroborate (0.69 g, 0.0015 mole) at −80°. The resulting suspension was stirred and allowed to warm up to −20°. The solution rapidly became blue and silver metal was deposited. After 3 h at −20° the silver metal was filtered off under nitrogen and the solvent removed in a nitrogen stream. Pumping at $10^{-4}$ mm for several hours removed occluded sulphur dioxide leaving analytically pure 1,3-diacetylferricenium tetrafluoroborate (Table 4).

Different behaviour was observed when the 1,2-diacetylferrocene silver fluoroborate complex was allowed to interact with liquid sulphur dioxide. Instead of the typical blue colouration due to ferricenium, a brown solution was produced and silver metal deposited as before. Filtration and subsequent removal of the solvent in vacuo gave a brown solid which was diamagnetic at room temperature. The C and H analyses are as expected for 1,2-diacetylferricenium tetrafluoroborate (Table 4).

The $^1$H NMR spectrum of this compound in liquid sulphur dioxide consisted of three main peaks. Two sharp singlets at $\tau$ 7.15 and $\tau$ 5.13 and a broad multiplet centred at $\tau$ 3.83, the ratio of intensities being 6/5/3 respectively. The $^1$H NMR spectrum of 1,2-diacetylferrocene in the same solvent is not very different from this[14], *i.e.* the protons of the methyl groups at $\tau$ 7.5 and the unsubstituted ring protons at $\tau$ 5.59. The remaining three protons on the substituted ring appear as a doublet ($\tau$ 4.975) and a triplet ($\tau$ 5.19).

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