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# ACID-CATALYSED KETONE REARRANGEMENTS OF t-BUTANOYL SUBSTITUTED $\eta^6$-ARENE-$\eta^5$-CYCLOPENTADIENYLIRON(II) CATIONS

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## Summary

The t-butanoyl substituent of $\eta^6$-benzene-$\eta^5$-t-butanoylcyclopentadienyliron(II) hexafluorophosphate rearranges to a 3-methylbutan-2-oyl group under the influence of electrophilic catalysts such as $AlCl_3$ or $CF_3SO_3H$. This typical rearrangement of $\alpha$-branched ketones has been studied in several acids, and the rates are compared to those for the analogous rearrangement of the uncomplexed t-butyl phenyl ketone. The presence of the $C_6H_6Fe^+$ group markedly increases the rate of reaction. $\eta^6$-t-Butanoylbenzene-$\eta^5$-cyclopentadienyliron(II) hexafluorophosphate was also found to undergo a similar rearrangement, but there was a major competing reaction involving loss of the t-butanoyl substituent. The presence of the (arene)$Fe^+$(cp) group causes a $10^4$–$10^5$ fold increase in the rate of the rearrangement.

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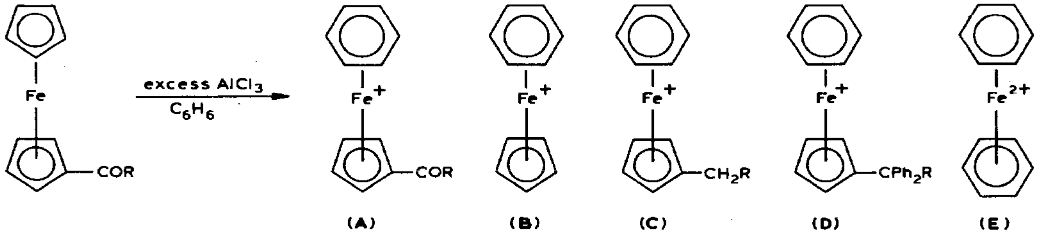
## Introduction

Aluminium chloride-induced cleavage of ferrocene in the presence of arenes is a well documented route to $\eta^6$-arene-$\eta^5$-cyclopentadienyliron(II) cations [1]. The behaviour of monoacylferrocenes in this reaction has been investigated by Astruc [2]. The major product is that of exchange of the unsubstituted cyclopentadienyl ring (**A**), the minor products being arene cations containing the unsubstituted Cp ring (**B**), alkyl substituted Cp rings via reduction of the keto function (**C**), and products arising from addition of arene molecules to the carbonyl carbon (**D**). Di-$\eta^6$-areneiron(II) dications (**E**) can also be detected in some cases. The distribution of products depends on the acylferrocene and arene used [2].



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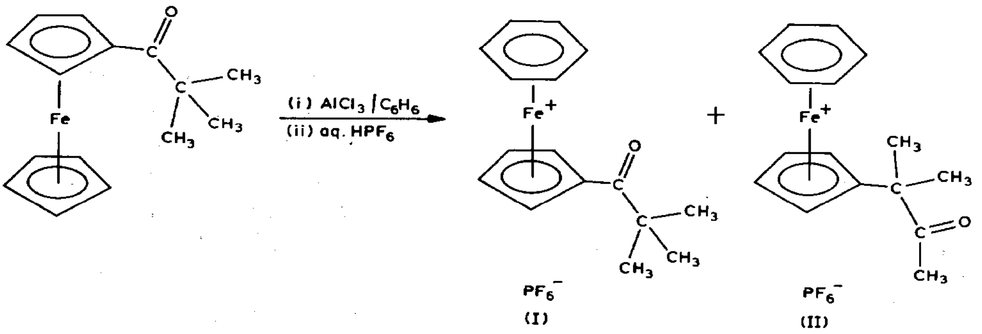
We recently had cause to synthesise the $\eta^6$-benzene cation containing a t-butanoyl substituted Cp ring, and found the reaction produced an unexpected by-product arising from the rearrangement of the t-butanoyl group. We subsequently investigated this rearrangement and the rearrangement of the t-butanoylarene-substituted analogue with a view to quantifying the effect of complexation on the rate of isomerisation.

## Discussion and results

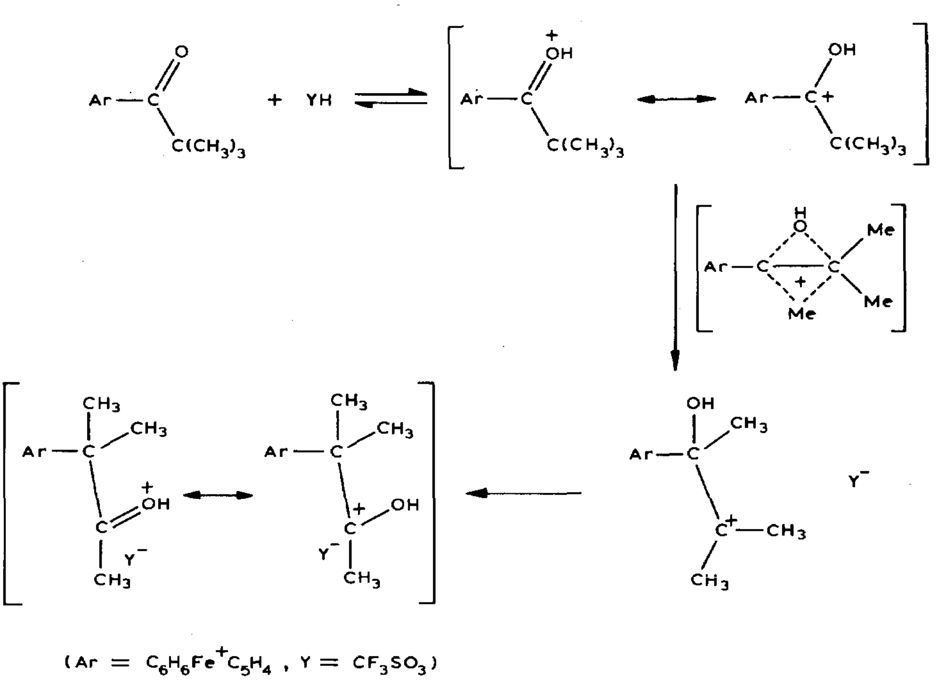
The expected arene complex (I) could be isolated from the reaction of t-butanoyl ferrocene with aluminium chloride in refluxing benzene. However, in addition the reaction mixture showed one major component (II) which did not correspond to the structure of any of the usual side products (**B**–**E**). Elemental analysis showed these two major products to be isomeric, $^1$H, $^{13}$C NMR and IR spectroscopy revealed the side-chain in the by-product to be the 3-methylbutan-2-oyl group, as shown.



The rearrangement of the t-butanoyl group was shown to occur after the cleavage of the unsubstituted Cp ring and formation of the cation, rather than on the ferrocene prior to reaction (vide infra).

Two different reaction times were used in the synthesis with the following results: Reaction time of 1 h giving a total yield of 48% (I/II 90/10); reaction time of 3 h giving a total yield of 55% (I/II 70/30). In each case an average of two determinations is stated.

Clearly increasing the reaction time above 1 h does not greatly influence the total yield but does increase the proportion of II, showing that I is rapidly formed and slowly converted into II. Similar rearrangements found for other $\alpha$-branched ketones are catalysed by Lewis acids or strong protic acids [3]. Thus, t-butyl phenyl ketone rearranges to 3-methyl 3-phenyl butan-2-one in 71% $HClO_4$ (91% at 24 h, 20°C) [4]. Isomer I dissolved in 71% $HClO_4$ and trifluoroacetic and (TFA) and could be recovered unchanged after 24 h. I dissolved in the much stronger trifluoromethanesulphonic acid ("triflic acid", $CF_3SO_3H$) to give intense purple solutions characteristic of *O*-protonated ferrocenyl ketones [5] (solutions of I in 71% $HClO_4$ and TFA were yellow). During 6 h at room temperature the purple colour faded to yellow, and examination of reaction mixtures by $^1$H NMR spectroscopy showed that conversion of I into II had occurred. Thus protic acids strong enough to protonate the keto- groups also effect the conversion I into II. The $^1$H NMR spectrum which appeared in the triflic acid solution of I was identical to that

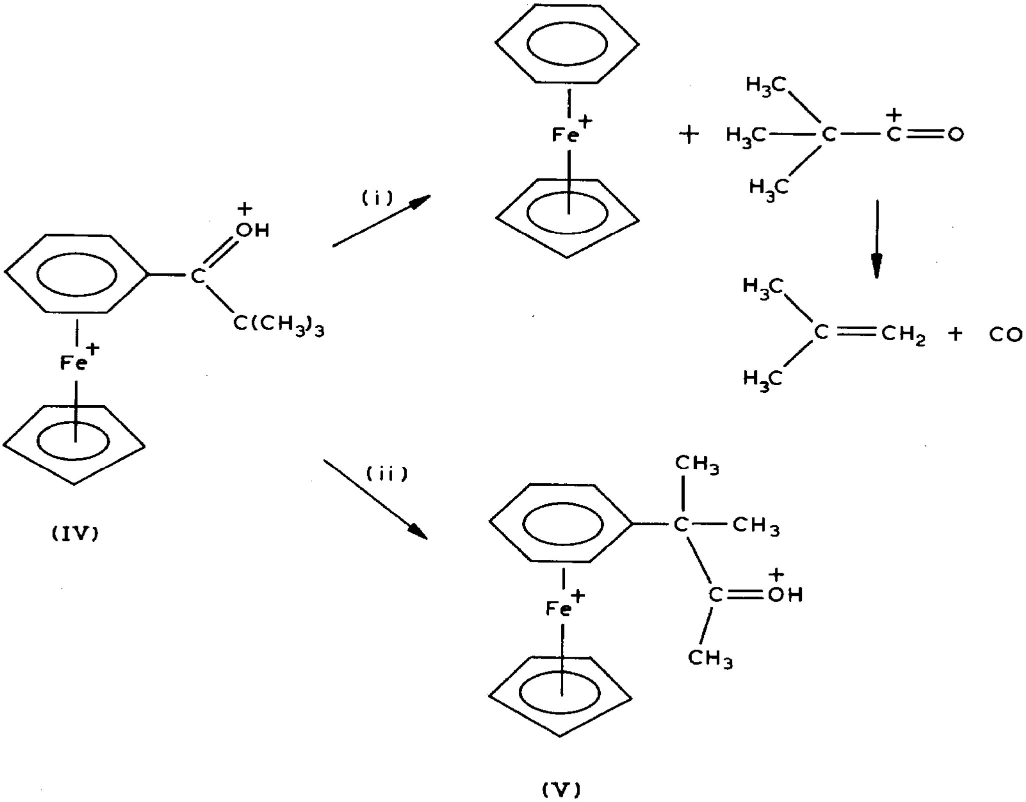


SCHEME 1

produced by pure II in triflic acid. I also dissolved in 98% $H_2SO_4$ to give a purple solution in which an identical rearrangement occurred, albeit more slowly. Simple first order rate constants calculated from the relative molar composition of reaction mixture, as measured by NMR, were $1.3 \times 10^{-4}$ $s^{-1}$ in triflic acid and $8.4 \times 10^{-6}$ $s^{-1}$ in 98% $H_2SO_4$ at 20°C. t-Butyl phenyl ketone has been reported [4] not to rearrange in 91% $H_2SO_4$ (same $H_0$ value as for 71% $HClO_4$) hence effects other than measured acidity are important. The arene cation does not rearrange in TFA or 71% $HClO_4$ as the carbonyl is not protonated in these media, the positive charge greatly lowering the basicity of the keto oxygen. On the other hand t-butyl phenyl ketone readily rearranged in triflic acid. The reaction was monitored by $^1H$ NMR and a value of $k_1$ or $6 \times 10^{-6}$ $s^{-1}$ was obtained. The arene cation I thus rearranged ~ 20 times faster than t-butyl phenyl ketone in triflic acid. The proposed mechanism for this type of rearrangement [6] is via a series of methyl shifts, see Scheme 1.

The increased rate for the arene cation arises from the strong tendency to increase the distance between the two positive charges. A more direct comparison with the uncomplexed ketone would be the t-butanoylarene cation rather than the t-butanoylcyclopentadienyl complex.

We synthesised this derivative (IV) from the corresponding $\eta^6$-neopentylbenzene complex (III) using $KMnO_4$ (after Sutherland et al. [7]). IV was formed in low yield due to considerable decomposition of product and/or starting material. However, we obtained enough material to examine its behaviour in $CF_3SO_3H$. IV dissolved in triflic acid to give a brown solution. The rearrangement was monitored by $^1H$ NMR by following the disappearance of the t-Bu signal at 1.16 ppm and the appearance of the $Me_2C$ and MeCO signals at 1.90 and 2.72 ppm respectively. However, as the



SCHEME 2

reaction proceeded it became apparent that the ratio of aromatic to aliphatic protons was increasing, showing that there was a competing process giving a second $\eta^6/\eta^5$ complex, since the complexed arene signal was almost unchanged.

Since no other rearranged side group could be detected, this was assigned to $\eta^6$-benzene-$\eta^5$-cyclopentadienyliron(II) hexafluorophosphate, which was subsequently detected by TLC examination of the reaction products. This product arises by cleavage of t-butanoyl cation from the protonated ketone. The latter can then decompose to give CO and isobutene, which accounts for the observed loss of hydrogen signals in the NMR.

Thus the overall reaction of IV in triflic acid is as shown in Scheme 2.

After all the starting material had disappeared the ratio of aromatic : aliphatic protons was 1 : 0.38, considerably different from that predicted for the simple rearrangement (1 : 0.9). The calculated ratio for a 50% mixture of V and $[C_6H_6Fe^+cp][PF_6^-]$ is 1 : 0.42, which suggests that the activation energies for steps (i) and (ii) are comparable. The NMR data were analysed in more detail, see Table 1. The first order rate constant for (ii) was found to be $(1.2 \pm 0.3) \times 10^{-4}\ s^{-1}$. From the decrease in the sum of the methyl resonances [t-Bu + MeCO + $Me_2C$], process (i) can be evaluated and an identical rate constant was obtained within experimental error.

TABLE 1 $^1$H [a] AND $^{13}$C NMR [b] CHEMICAL SHIFTS FOR $(C_6H_6)Fe^+C_5H_4X$ DERIVATIVES (X = t-BuCO (I), $C(CH_3)_2COCH_3$ (II), EtCO (VI)) AND $C_6H_5$-$YFe^+C_5H_5$ DERIVATIVES (Y = $CH_2CMe_3$ (III), t-BuCO (IV), $C(CH_3)_2COOH_3$ (V))

| Compound | Solvent | $^1$H NMR | | | | | $^{13}$C NMR | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $C_6H_6$ | H(2)H(5) | H(3)H(4) | Others | | $C_6H_6$ | C(1) | C(2)C(5) | C(3)C(4) | CO | | Others | |
| I | $CD_3CN$ | 5.95s | 5.17m | 4.90m | t-Bu | 0.95s | 89.19 | | 77.08 | 77.08 | 205.93 | t-Bu *Me* | 25.78, | 44.54 |
| I | $CF_3CO_2H$ | 5.95s | 5.17m | 4.85m | t-Bu | 0.85s | – | – | – | – | – | – | | |
| I | $CF_3SO_3H$ | 6.25s | 5.80m | 5.50m | t-Bu | 1.37s | | | | | | | | |
| I | 98% $H_2SO_4$ | 6.20s | 5.60m | 5.30m | t-Bu | 1.32s | – | – | – | – | – | – | | |
| II | $CD_3COCD_3$ | 5.90s | 4.80m | 4.80m | $Me_2C$ | 1.05s | 88.21 | 104.91 | 75.52 | 74.30 | 208.14 | MeCO | 24.65 | |
| | | | | | MeCO | 1.45s | | | | | | $Me_2C$ | 23.94 | |
| | | | | | | | | | | | | $Me_2C$ | 46.59 | |
| II | $CF_3SO_3H$ | 6.06s | 4.85m | 4.85m | $Me_2C$ | 1.58s | | | | | | | | |
| | | | | | MeCO | 2.50s | – | – | – | – | – | – | | |
| II | 98% $H_2SO_4$ | 6.14s | 5.16m | 5.16m | $Me_2C$ | 1.80s | | | | | | | | |
| | | | | | MeCO | 2.60s | | | | | | | | |
| VI | $CD_3CN$ | 6.08s | 5.30m | 4.95m | $CH_3$ | 0.9t | | | | | | | | |
| | | | | | $CH_2$ | 2.60q | – | – | – | – | – | – | | |
| VI | $CF_3CO_2H$ | 5.90s | 5.20m | 4.88m | $CH_3$ | 0.80t | | | | | | | | |
| | | | | | $CH_2$ | 2.55q | – | – | – | – | – | – | | |
| VI | $CF_3SO_3H$ | 6.28s | 5.76m | 5.50m | $CH_3$ | 1.30t | | | | | | | | |
| | | | | | $CH_2$ | 3.15q | – | – | – | – | – | – | | |

| | | $^1$H NMR | | | | $^{13}$C NMR | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $C_5H_5$ | arene | Others | | $C_5H_5$ | C(1) | C(2)C(6) | C(3)C(5) | C(4) | CO | Others | |
| III | $CD_3COCD_3$ | 4.65s | 5.90s | $CH_3$ | 0.42s | 77.35 | 105.50 | 88.08 | 89.92 | 87.34 | – | t-Bu *Me* | 28.79 |
| | | | | $CH_2$ | 2.30s | | | | | | | | 32.59 |
| IV | $CD_3COCD_3$ | 4.77s | 6.13m | $CH_3$ | 0.84s | 78.72 | 104.34 | 87.60 | 87.38 | 89.29 | 207.39 | t-Bu *Me* | 26.81 |
| | | | | | | | | | | | | | 45.36 |
| IV | $CF_3SO_3H$ | 4.83s | 6.22m | $CH_3$ | 1.17s | | | | | | | | |
| V | $CD_3COCD_3$ | 4.50s | 5.80s | $Me_2C$ | 0.65s | | | | | | | | |
| | | | | MeCO | 1.12s | | | | | | | | |
| | $CF_3SO_3H$ | 4.75 [c] | 6.27 [c] | $Me_2C$ | 1.90s | | | | | | | | |
| | | | | MeCO | 2.72s | | | | | | | | |

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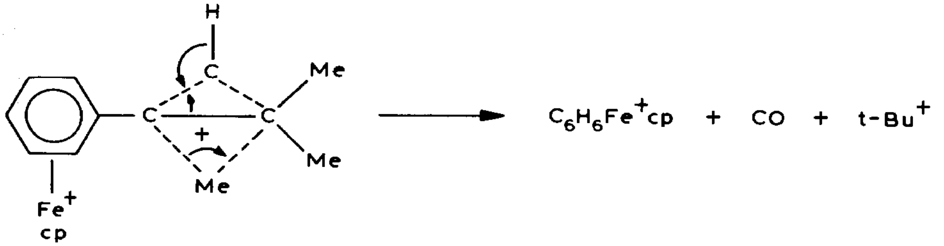
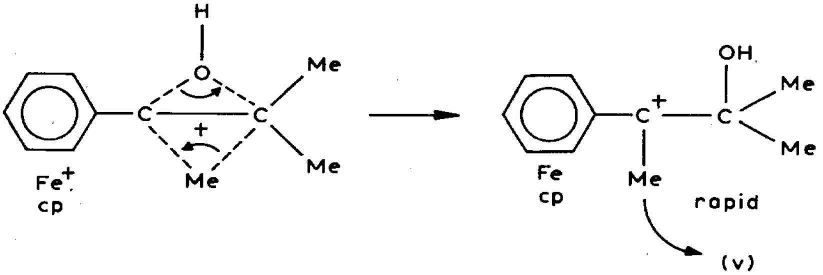
[a] In ppm from external TMS, s = singlet, t = triplet, q = quartet, m = multiplet. [b] In ppm from TMS, solvent $CH_3CN$. [c] $\delta$ approximate as presence of three $\eta^6/\eta^5$ cations gives broad singlets for cp and arene.

Thus it appears that the first carbocation formed decomposes with equal facility to V and [$C_6H_6Fe^+cp$].



(i)



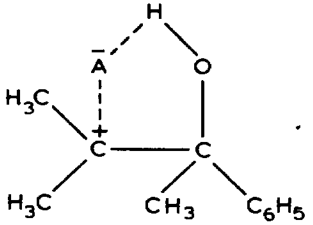
(ii)

It is noteworthy that the t-BuCO group is not cleaved from the Cp ring. We suspect that the higher electron density of the latter inhibits electron transfer to the $C_6H_5Fe^+cp$ moiety. The rate of rearrangement of IV is thus very similar to that of I. However the $k_1$ values include the equilibrium constant ($K$) for carbonyl protonation. IV is likely to be a much weaker base than I. The colours of the reaction mixtures support this. I in $CF_3SO_3H$ gives an intense purple colour whereas IV forms brown solutions. Other $\eta^6$-arene-$\eta^5$-cp$Fe^{II}$ cations with COR substituents on the arene ring which are likely to be more basic than IV, e.g. $\eta^6$-fluorenone and $\eta^6$-diphenyl ketone complexes, form intense purple solutions in $CF_3SO_3H$. Whilst p$K$ values are not available for I and IV, the acyl group on the Cp ring in I is likely to be 3–4 orders of magnitude more basic than when on the arene ring in IV. Ferrocenyl ketones are ~ five orders of magnitude more basic than corresponding aryl systems, as shown by the p$K_a$ values of $-2.80$ for acetylferrocene [8] compared to $-6.15$ for acetophenone [3].

The ketone-substituted arene cations described here are obviously very much weaker bases than their ferrocenyl counterparts. TFA ($H_o$ $-2.77$ to $-4.4$) [10] is strong enough to protonate most $\alpha$-ferrocenyl ketones whereas the replacement of a Cp anion by a $\eta^6$-arene to give a cation, results in a large decrease in basicity such that 98% $H_2SO_4$ ($H_o = -10.27$) [11] is required to achieve a reasonable degree of protonation of I. (98% $H_2SO_4$ is in fact strong enough to diprotonate 1,1-diacylferrocenes [12].).

Taking the above arguments into consideration, it is likely that the complexed t-butyl phenyl ketone (IV) rearranges some $10^4$–$10^5$ times as fast as the uncomplexed analogue, reflecting the extremely large effect of the $Fe^+cp$ moiety on the reaction.

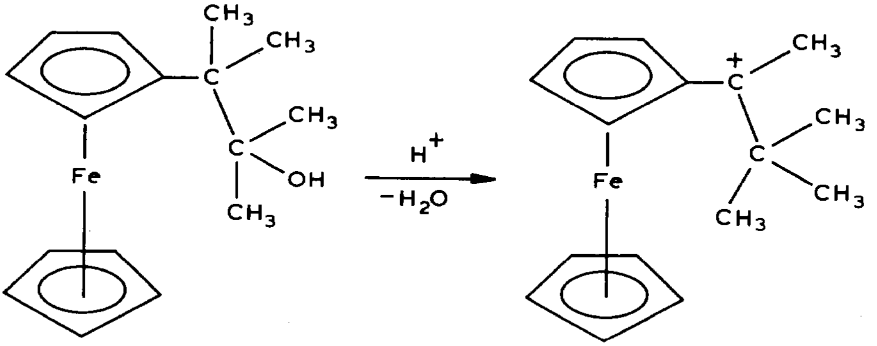
It has been suggested that the acid catalysed rearrangement of t-butyl phenyl ketone involves a cyclic ester intermediate which is not hydrolysed to the product until the reaction mixture is diluted with water [6]:



For arene cations I, IV, and t-butyl phenyl ketone in triflic acid no such intermediate was detected by NMR. In triflic acid such bridged species would be unlikely due to the low nucleophilicity of the triflate ion.

We also synthesised the propanoyl analogue of I (VI) and found no rearranged by-products from the $AlCl_3$ catalysed synthesis. The propanoyl analogue dissolved in triflic acid to give an intense purple solution in which again no rearrangement was detected. This is in keeping with the general features of such reactions, in which $\alpha$ branching is required for rearrangement. Thus only ketone → ketone, aldehyde → ketone and not ketone → aldehyde [3] rearrangements are found. As with I, dissolution in TFA caused no protonation of the keto function, as evident from the pale yellow colour.

$\alpha$-Ferrocenylcarbonium ions are well known stable species, stabilisation of the positive charge being via the iron $e_{2g}$ orbitals. Indeed, where possible, the reverse of the rearrangement I → II and IV → V occurs, moving the positive charge towards the iron atom [13,14].



It was observed that t-butyl ferrocenyl ketone did not rearrange in triflic acid; extensive oxidation was apparent after ~ 6 h. Whilst both systems contain a $d^6$ electron configuration, the positive charge on the iron atom in the $\eta^6$-arene complexes causes quite different behaviour in the acid catalysed rearrangements of the two types of complex.

## Experimental

Benzene was dried over sodium. Aluminium chloride was used from freshly opened bottles or sublimed before use. Triflic acid was purchased from 3M Chemicals.

Ferrocenyl ketones were prepared by standard Friedel–Crafts reactions. $^1$H NMR spectra were run on a Varian EM360 spectrometer and $^{13}$C NMR on a Bruker Spectro-spin WP80 instrument (reference external TMS). Microanalyses were obtained from the Analytical Department, University of Manchester.

### *$\eta^6$-Benzene-$\eta^5$-t-butanoylcyclopentadienyliron hexafluorophosphate (I) and its rearrangement product (II)*

t-Butanoylferrocene [15] and aluminium chloride (1 : 4 mol ratio) were refluxed in dry benzene for 1 or 3 h. After cooling and quenching with ice water the organic phase was discarded and the aqueous phase filtered and washed with ether. The products were precipitated from the aqueous phase with 75% hexafluorophosphoric acid solution, filtered and dried. After drying, the crude product was washed with dichloromethane until the solvent was almost colourless. The residue was dissolved in acetone/acetonitrile (1 : 1) and reprecipitated with ether to give pure isomer I. (The yields are given in the text). M.p. > 200°C dec $\nu$(CO) (Nujol) 1675 cm$^{-1}$. Found: C, 44.4; H, 4.5. $C_{16}H_{19}F_6FeOP$ calc.: C, 44.9; H, 4.4%.

Ether was added to the $CH_2Cl_2$ layer to precipitate isomer II which contained 10–30% of isomer I as determined from $^1$H NMR spectra. Pure samples of II were obtained after chromatography on alumina using acetone as the eluant. M.p. 150–154°C dec $\nu$(CO) (Nujol) 1700 cm$^{-1}$. Found: C, 44.2; H, 4.5. $C_{16}H_{19}F_6FeOP$ calc.: C, 44.9; H, 4.4%.

### *$\eta^6$-Neopentylbenzene-$\eta^5$-cyclopentadienyliron(II) hexafluorophosphate (III)*

Neopentylbenzene (10 g, 0.068 mol), ferrocene (12.6 g, 0.068 mol), aluminium chloride (27.3 g, 0.2 mol), aluminium (3.5 g, 0.14 mol) and water (1.2 g, 0.068 mol) were refluxed overnight in methylcyclohexane (~ 150 cm$^3$). After cooling and quenching with ice water, the organic phase was discarded and the aqueous layer filtered. After washing the latter with ether, the product was precipitated by the addition of 75% aq. $HPF_6$. The product was filtered, dried, dissolved in acetone and reprecipitated by the addition of excess ether. Yield 14 g (50%). The analytical sample was prepared by chromatography on alumina with acetone. M.p. 145–148°C. Found: C, 47.6; H, 5.2. $C_{16}H_{21}FeF_6P$ calc.: C, 46.4; H, 5.1%.

### *$\eta^6$-t-Butanoylbenzene-$\eta^5$-cyclopentadienyliron(II) hexafluorophosphate (IV)*

Finely ground III (6 g, 0.014 mol) was refluxed with potassium permanganate (20 g, 0.126 mol) in water (80 cm$^3$) for 2 h with high speed stirring. After cooling, the excess permanganate was removed by addition of sodium thiosulphate and the solution filtered through Celite. $HPF_6$ (5 cm$^3$, 75%) was added and the aqueous phase extracted with dichloromethane (100 cm$^3$). The organic phase was dried over anhydrous sodium sulphate and the solvent removed in vacuo. The residue was chromatographed on alumina with acetone which eluted unreacted starting material. The product was eluted with acetone/methanol (70 : 30 v/v) and isolated by precipitation with ether. Yield 0.3 g (5%). M.p. 131–133°C, $\nu$(CO) (Nujol) 1680 cm$^{-1}$. Found: C, 44.5; H, 4.5. $C_{16}H_{19}FeF_6OP$ calc.: C, 44.9; H, 4.4%.

An attempted autooxidation of III as described by Sutherland [7] for the $\eta^6$-fluorene complex failed.

### *$\eta^6$-Benzene-$\eta^5$-propanoylcyclopentadienyliron(II) hexafluorophosphate (IV)*

This derivative was prepared in 26% yield using an identical method to that described for I (reaction time 3 h). The only other product isolated was $\eta^6$-benzene-$\eta^5$-cyclopentadienyliron(II) hexafluorophosphate (6%). The pure ketone was obtained by washing the crude material with $CH_2Cl_2$, dissolving the residue in acetone and precipitating with ether. M.p. 162.4°C dec. $\nu$(CO) (Nujol) 1685 $cm^{-1}$. Found: C, 40.7; H, 3.7. $C_{14}H_{15}F_6FeOP$ calc.: C, 42.0; H, 3.8%.

### *Kinetics*

I was dissolved in $CF_3SO_3H$ to give 0.2–0.5 *M* solution which was transferred to an NMR tube at room temperature $20 \pm 1.0$. The reaction was monitored by measuring the decrease of the t-butyl signal at 1.37 ppm in I and the increases in the *gem* dimethyl signal at 1.58 ppm and acetyl methyl group at 2.50 ppm in II. First order rate constants were calculated from the data in the usual way. The rearrangement of IV was followed in a similar manner.

### *Product identification for rearrangement IV → V*

After the complete disappearance of IV the triflic acid reaction mixture was diluted with water ($\sim 5$ $cm^3$) and extracted with $CH_2Cl_2$ (10 $cm^3$). The organic phase was dried and evaporated to dryness. V was detected by $^1H$ NMR of the residue in acetone-$d_6$. Examination by TLC (silica plates, eluant $MeNO_2$) showed two spots of roughly equal intensity. The spot with the lowest $R_f$ value of 0.78 was assigned to V, the higher $R_f$ spot at 0.84 was assigned to $\eta^6$-benzene-$\eta^5$-cyclopentadienyliron(II)$PF_6$. A standard solution of the unsubstituted cation gave an identical $R_f$ value.

## References

1 For an up-to-date review see D. Astruc, Tetrahedron, 39 (1983) 4027.
2 D. Astruc and R. Dabard, Tetrahedron, 32 (1976) 245.
3 For a discussion of the reaction see A. Fry in B.S. Thyagarajan (Ed.), Mechanisms of Molecular Migrations, Vol. 4, Wiley, New York, 1971, p. 113.
4 T.E. Zalesskaya and T.B. Remizova, Zh. Obsch. Khim., 33 (1963) 3802.
5 G. Neshvad, R.M.G. Roberts and J. Silver, J. Organomet. Chem., 260 (1984) 319.
6 T.E. Zalesskaya, Zh. Obsch. Khim., 16 (1946) 1813.
7 C.C. Lee, K.J. Demchuk, U.S. Gill and R.G. Sutherland, J. Organomet. Chem., 247 (1983) 71.
8 E.M. Arnett and R.D. Bushick, J. Org. Chem., 27 (1962) 111.
9 R. Stewart and K. Yates, J. Am. Chem. Soc., 80 (1958) 6355.
10 J.B. Milne in J.J. Lagowski (Ed.), The Chemistry of Non-Aqueous Solvents, Wiley, New York, 1978, Ch. 1.
11 R.S. Ryabova, I.M. Medvetskaya and M.I. Vinnik, Russ. J. Phys. Chem., 40 (1966) 182.
12 G. Neshvad, R.M.G. Roberts, and J. Silver, J. Organomet. Chem., 236 (1982) 349.
13 C.C. Lee, S.C. Chen, W.J. Pannekoek and R.G. Sutherland, J. Organomet. Chem., 118 (1976) C47.
14 S. Brown, T.S. Abram and W.E. Watts, J. Organomet. Chem., 97 (1975) 42.
15 T.S. Abram, T.D. Turbitt and W.E. Watts, J. Chem. Soc. Perkin Trans. I, (1977) 1536.