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# REACTIONS OF FLUORINATED KETONES WITH FERROCENES

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## Summary

Ferrocene reacts with hexa- or penta-fluoroacetone, either directly (180°/15 days) or with a catalyst ($AlCl_3$/20°/24 h), to give fluorinated 2-ferrocenylpropan-2-ols, $C_5H_5FeC_5H_4C(CF_3)(CF_2X)OH$ (X = F or H). Acetyl- or benzoylferrocene react similarly with hexafluoroacetone in the presence of $AlCl_3$ to give the corresponding 1,1'-derivatives, $RC(O)C_5H_4FeC_5H_4C(CF_3)_2OH$ (R = Me or Ph).

## Introduction

Recent reports of the reactions of hexafluoroacetone with Group VIII metal cyclopentadienyl derivatives [1,2], and earlier reports of condensations of this reagent with aromatic species [3], prompted us to examine the reactions of some fluorinated ketones with ferrocene derivatives. Ketones condense with ferrocene in the presence of a Lewis acid, affording carbinols, olefins or oligomeric products, the nature of the products depending on the conditions employed [4]. While condensations of ferrocene with chloroaldehydes have been reported [4,5], to our knowledge no reactions with fluorinated ketones have been noted.

## Results and discussion

Following our previous observation of the direct insertion of hexafluoroacetone (HFA) into a C—H bond of the cyclopentadienyl group in $(C_5H_5)Ru(PPh_3)_2[C_2(CO_2Me)_2H]$ [1], ferrocene was heated with HFA in several solvents; the product was separated from unreacted ferrocene by chromatography (alumina), and shown to be the carbinol Ia. Better yields were obtained using more polar solvents such as 1,2-dimethoxyethane. The same product was obtained in reactions run at room temperature when $AlCl_3$ was present as cata-

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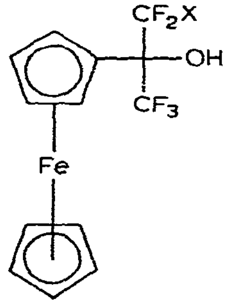
TABLE 1

REACTIONS OF FLUORINATED KETONES WITH FERROCENES[a]

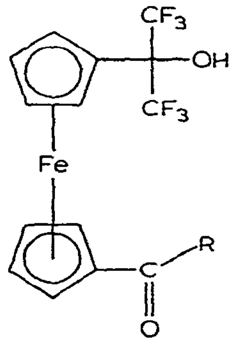
| Ferrocene | Ketone | Ketone/ ferrocene (mole ratio) | Solvent | Temperature (°C) | Time (days) | Condensation product (%) | Recovered ferrocene (%) |
|---|---|---|---|---|---|---|---|
| FcH | HFA | 1.0 | Hexane | 120 | 2 | Ia (1.7) | 88.7 |
| FcH | HFA | 2.0 | DME | 120 | 11 | Ia (9.5) | 67 2 |
| FcH | HFA | 2.0 | DME | 180 | 15 | Ia (87.3) | 11.5 |
| FcH | HFA | 2.0 | P.E. | 180 | 17 | Ia (35.3) | 64.0 |
| FcH | HFA | 1.0 | $CH_2Cl_2$[b] | ambient | 1 | Ia (19.9) | 69.0 |
| FcAc | HFA | 1.5 | $CH_2Cl_2$[b] | ambient | 4 | IIa (45.7) | 36.0 |
| FcCOPh | HFA | 1.5 | $CH_2Cl_2$[b] | ambient | 3 | IIb (20.0) | 61.5 |
| FcH | PFA | 1.0 | $CH_2Cl_2$[b] | ambient | 1 | Ib (10.5) | 75.3 |
| FcH | PFA | 2.2 | DME | 180 | 7 | Ib (16.7) | 77.5 |
| FcH | $Me_2CO$ | ca. 2% FcH | $Me_2CO$ | 180 | 7 | | 93.0 |
| FcH | $Ph_2CO$ | 1.2 | DME | 180 | 6 | | 83.0 |
| FcH | $[(CF_3)_2CF]_2CO$ | 1.0 | DME | 180 | 11 | | 85.0 |

[a] No attempt was made to obtain optimum *yields* in the above reactions. Abbreviations: Fc, ferrocenyl; HFA, hexafluoroacetone; PFA, pentafluoroacetone; DME, 1,2-dimethoxyethane; P.E., light petroleum. [b] With added aluminium chloride as catalyst. [c] Yields are based on the initial amount of the ferrocene taken.

lyst. Similar reactions occurred between HFA and acetyl- and benzoyl-ferrocenes to give IIa and IIb; pentafluoroacetone (PFA) and ferrocene also reacted, both thermally and under Friedel—Crafts conditions, to give Ib. Reaction conditions and yields are summarised in Table 1.



(I) a, X = F
b, X = H



(II) a, R = Me
b, R = Ph

We were not able to effect a thermal condensation between ferrocene and heptafluoroisopropyl ketone, $[(CF_3)_2CF]_2CO$, possibly because of steric effects; no products were obtained from reactions using acetone or benzophenone, although in the presence of $AlCl_3$, the former yields oligomeric species [4].

Only 1/1 condensation products were found from both types of reaction, even when excess fluoroketone was employed. In the case of the acetylferrocene—HFA reaction, a trace of a second red product was obtained. This gave a molecular ion at *m/e* 394, indicating that it may have been a homo-disubstituted isomer of IIa ($M^+$, $m/e$ 394), but not enough material was obtained for full characterisation.

The products are all stable crystalline solids which can be sublimed readily, although IIb was initially isolated as an oil, which solidified after distillation.

While the $AlCl_3$-catalysed condensation of the fluoroketones with ferrocenes probably occurs by electrophilic attack on the latter by an activated complex of the type $(R_f)_2\overset{+}{C}\cdots\overset{-}{O}AlCl_3$, as with aromatic compounds [3,6], we cannot be as certain about the thermal reaction. Two modes of attack can be envisaged either *exo* or *endo*, for both the thermal and Lewis-acid catalysed condensations. If *endo*, the reaction may proceed via an iron-coordinated intermediate, followed by migration of the entering group from the metal to the ring.

The stability of the $C(CF_3)_2OH$ group towards strongly acidic, basic, oxidising and reducing reagents has been demonstrated previously both in aromatic analogues of Ia [6,7], and for a metal derivative [8]. The formation of IIa by reaction of Ia with acetyl chloride and $AlCl_3$ in refluxing dichloromethane indicates a similar stability for the ferrocene derivatives. The resistance of Ia to ether formation under acid conditions ($Et_3O^+BF_4^-/Et_2O$; EtOH/AcOH) demonstrates the highly acidic nature of the hydroxyl proton; unlike other $\alpha$-ferrocenylcarbinols [9,10], Ia was inert to refluxing aniline, and was not alkylated by MeMgI in refluxing benzene.

These results may be due to the destabilising effect of the electronegative $CF_3$ groups on the incipient $\alpha$-ferrocenylcarbonium ion. Attempts to observe this cation by looking at the NMR spectrum of Ia in $CF_3CO_2H$ were unsuccessful due to the rapid formation of a green paramagnetic solution, from which Ia could be recovered, however.

## Experimental

Spectra were recorded on Perkin—Elmer 457 (infrared), Varian Associates HA-100 at 100 ($^1H$ NMR) and 94.1 MHz ($^{19}F$ NMR), and AEI MS902 (mass spectra) instruments. Solvents were dried and distilled before use in reactions, which were carried out under nitrogen. Light petroleum refers to a fraction b.p. 40—60°.

### *2-Ferrocenylhexafluoropropan-2-ol (Ia)*

*(a) Thermal condensation.* Ferrocene (1.86 g, 10 mmol), HFA (20 mmol) and 1,2-dimethoxyethane (40 ml) were charged into a Carius tube and heated for 15 days at 180°. After cooling, the tube was opened, the solution filtered and evaporated (rotary-evaporator) and the residue transferred to an alumina column using the minimum of benzene. Light petroleum eluted unreacted ferrocene (0.215 g) as the first fraction; ether eluted the product as the second and final fraction, which was evaporated to give golden plates of Ia (3.073 g, 87.3%) m.p. 99—101°, subliming at 80°/0.02 mm. (Found: C, 43.9; H, 2.95; F, 32.85. Mol. wt. 352. $C_{13}H_{10}F_6FeO$ calcd.: C, 44.3; H, 2.85; F, 32.4%. Mol. wt. 352.) IR: $\nu$(max) at 3515s (br) (OH); 1300—1200s (br) (C—F); 1100, 1000, 850, 825 $cm^{-1}$ (ferrocenyl). $^1H$ NMR ($\tau$, $CS_2$): 6.84s (br) (1H, OH) collapsing on addition of $D_2O$; 5.80s (5H, $C_5H_5$), 5.72t, 5.68m (4H, $C_5H_4$). $^{19}F$ NMR: 75.00s (br) ppm ($CF_3$).

*(b) Friedel—Crafts reaction.* A Carius tube was charged with ferrocene (5.58 g, 30 mmol), HFA (30 mmol), aluminium trichloride (2.67 g, 20 mmol) and dichloromethane (50 ml) and the deep-blue solution shaken at ambient temperature for 1 day. The tube contents were then poured onto crushed ice, treated with *l*-ascorbic acid to reduce the ferricinium species present, and extracted with dichloromethane. The organic extract was dried ($MgSO_4$), after washing with saturated aqueous $NaHCO_3$, evaporated down and the residue chromatographed on alumina to afford unreacted ferrocene (3.85 g) and the product Ia (2.10 g, 19.9%).

### *2-Ferrocenylpentafluoropropan-2-ol (Ib)*

*(a) Thermal condensation.* Ferrocene (2.00 g, 10.75 mmol) and PFA (24 mmol) in 1,2-dimethoxyethane (50 ml) were heated in a Carius tube at 180° for 7 days, then processed as above to afford recovered ferrocene (1.55 g) eluted with benzene, and the product, eluted with 2/1 benzene/ether. Sublimation at 90°/0.05 mm afforded yellow solid Ib (0.60 g, 16.7%), m.p. 70—71°. (Found: C, 46.9; H, 3.3; F, 28.5. Mol. wt., 334; $C_{13}H_{11}F_5FeO$ calcd.: C, 46.7; H, 3.3; F, 28.45%. Mol. wt., 334.) IR: $\nu$(max) at 3520s (br) (OH); 1280—1180s (br) (C—F); 1095, 1005, 850, 840, 830 cm$^{-1}$ (ferrocenyl). $^1$H NMR ($\tau$, $CDCl_3$): 7.03s (1H, OH), collapsing on addition of $D_2O$; 5.86s (5H, $C_5H_5$), 5.78t, 5.68m (4H, $C_5H_4$); 4.16dd as a triplet (1H, —$CHF_AF_B$, $J(HF_A)$ 55, $J(HF_B)$ 54 Hz). $^{19}$F NMR: 74.94dd as pseudotriplet (3F, $CF_3$, $J(CF_3$—$F_A)$ 10, $J(CF_3$—$F_B)$ 8 Hz); 126.25, $F_A$ portion of $F_AF_B$ spectrum as two pairs of doublets of quartets [1F, $CH\underline{F}_AF_B$, $J(F_AF_B)$ 292, $J(F_AH)$ 55, $J(F_ACF_3)$ 10 Hz]; 130.45 ppm, $F_B$ portion of $F_AF_B$ spectrum as two pairs of doublets of quartets [1F, $CHF_A\underline{F}_B$, $J(F_AF_B)$ 292, $J(F_BH)$ 54, $J(F_BCF_3)$ 8 Hz]. Irradiation at 74.94 ppm ($CF_3$) caused collapse of the quartet appearance of the eight quartets that constituted the $F_AF_B$ spectrum. The measured intensity of the AB spectrum reduced to the initial AB 4 line spectrum was 1.2/3.9/4.0/1.0; calculated intensity, 1.0/3.9/3.9/1.0.

*(b) Friedel—Crafts reaction.* Ferrocene (3.72 g, 20 mmol), PFA (20 mmol), aluminium chloride (2.87 g, 20 mmol) and dichloromethane were charged into a Carius tube and the deep-blue solution shaken at ambient temperature for 1 day and then processed as above to afford recovered ferrocene (2.8 g) and the product Ib (0.70 g, 10.7%).

### *1-(2-Hydroxyhexafluoroisopropyl)-1′-acetylferrocene (IIa)*

*(a) From acetylferrocene.* Acetylferrocene (2.28 g, 10 mmol), HFA (15 mmol), aluminium chloride (2.67, 20 mmol) and dichloromethane (75 ml) were charged into a Carius tube, the purple solution shaken for 4 days at ambient temperature and then quenched on ice and processed as above. Chromatography (alumina) afforded a trace of red substance eluted with toluene (molecular ion at *m/e* 394), followed by unreacted acetylferrocene (0.82 g) eluted with dichloromethane. The product was eluted with 1/1 dichloromethane/acetone, and was sublimed (100°/0.01 mm) to give pure red IIa (1.80 g, 45.7%), m.p. 104—106°. (Found: C, 45.85; H, 3.05; F, 29.0. Mol. wt., 394. $C_{15}H_{12}F_6FeO_2$ calcd.: C, 45.7; H, 3.05; F, 28.9%. Mol. wt., 394.) IR: $\nu$(max) at 3100s (br) (OH, intramolecularly associated), 1640s (br) (CO); 1300—1200s (br) (C—F); 1060, 1050, 1030, 850, 830 cm$^{-1}$ (ferrocenyl). $^1$H NMR ($\tau$, $CDCl_3$):

7.63s (3H, $CH_3$); 5.67m (2H), 5.57t (2H), 5.37t (2H), 5.10t (2H), ($C_5H_4$, $A_2B_2$ patterns); 5.24s (1H, OH), collapsing on addition of $D_2O$. $^{19}F$ NMR: 75.21s ppm ($CF_3$).

*(b) From 2-ferrocenylhexafluoropropan-2-ol (Ia).* 2-Ferrocenylhexafluoropropan-2-ol (Ia, 0.352 g, 1 mmol) was refluxed in dichloromethane with aluminium chloride (0.133 g, 1 mmol) and acetyl chloride (0.5 ml) for two hours. The purple solution was then quenched on crushed ice and processed as above. Chromatography on alumina afforded unreacted Ia (0.12 g) (eluted with dichloromethane), while 50/1 dichloromethane/acetone eluted the product IIa (0.07 g, 18.9%).

### *1-(2-Hydroxyhexafluoroisopropyl)-1'-benzoylferrocene (IIb)*

Benzoylferrocene (3.90 g, 10 mmol), HFA (15 mmol), aluminium chloride (2.67 g, 20 mmol) and dichloromethane (100 ml) were charged into a Carius tube and the resulting deep purple solution was shaken for 3 days and then processed as above. Chromatography on alumina afforded recovered benzoylferrocene (2.40 g) (eluted with 2/1 toluene/dichloromethane), and the product as a red oil (eluted with dichloromethane). This had b.p. 180°/0.25 mm, and solidified after distillation to give red IIb (0.91 g, 20%), m.p. 82—83° (from $CS_2$). (Found: C, 52.5; H, 3.0; F, 24.5. Mol. wt., 456. $C_{20}H_{14}F_6FeO_2$ calcd.: C, 54.65; H, 3.05; F, 25.0%. Mol. wt., 456.) IR (thin film): $\nu$(max) at 3230vs (br) (OH, intramolecularly associated); 1630s (CO); 1300—1200s (br) (C—F); 1060, 1040, 1030, 860, 850, 840 (ferrocenyl); 740, 710 $cm^{-1}$ (Ph). $^1H$ NMR ($\tau$, $CS_2$): 5.88m (2H), 5.78t (2H), 5.42t (2H), 5.12m (2H) ($C_5H_4$, $A_2B_2$ patterns); 3.72s (1H, OH), collapsing on addition of $D_2O$; 2.7—2.35m (3H), 2.30—2.05m (2H) ($C_6H_5$). $^{19}F$ NMR: 74.81s ppm ($CF_3$).

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