*Journal of Organometallic Chemistry*, 346 (1988) 67–90
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# Nucleophilic additions to cyclopentadienyliron complexed substituted benzenes hindered at the *ortho* positions with one or two methyl groups

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(Received October 5th, 1987)

## Abstract

Reaction of $NaBH_4$ with CpFe complexed 2-$CH_3C_6H_4X$, with X = $NO_2$, CN, $SO_2PhCH_3$-*p* or Cl (I, II, III or IV, respectively) resulted in the *exo*-addition of the hydride ion a C(2), C(3), C(4), C(5) and C(6), with reaction at C(6) to give the *ortho*-6 adduct as the major product. Similarly, reaction of the cyanide ion with I, II or III (treatment of $CN^-$ with IV resulted in substitution to give II), or the acetonyl anion with I, II, III or IV, gave only *o*-addition, with the *ortho*-6 adduct as the sole or predominant product. These results clearly suggested a steric hindrance effect by the 2-methyl group, with the C(6) position, the unhindered *o*-position to the electron-withdrawing substituent X, as the preferred site of reaction to give the major product. Analogous reactions of $NaBH_4$ with CpFe complexed 2,6-$(CH_3)_2C_6H_3X$, with X = $NO_2$, CN, $SO_2PhCH_3$-*p* or Cl (V, VI, VII or VIII, respectively) resulted in hydride additions at the *o*-, *m*- and *p*-positions. Since both *o*-positions at C(2) and C(6) were hindered by methyl groups, relatively greater amounts of *m*- and *p*-products were formed, with the *m*-adduct obtained in the greatest amount. In the addition of the cyanide ion to V, VI or VII, or the acetonyl anion to V, VI, VII or VIII, the *o*-adduct was the dominant product, but formation of some *m*- and *p*-products were also observed.

Considering the relative bulkiness of the cyanide ion, the acetonyl anion and the borohydride ion, it was concluded that other factors beside steric effect, such as electronic and free valency effects, as well as the nature of the substituents and the nature of the nucleophile, all could play a role in giving rise to the overall product distribution in these nucleophilic addition reactions.

## Introduction

Nucleophilic additions to organotransition metal cations containing unsaturated hydrocarbon ligands, including hydride additions to some $\eta^6$-arene-$\eta^5$-cyclopenta-

dienyliron cations, have been reviewed in 1978 [1]. For example, the work of Watts and coworkers [2–5] showed that in the hydride addition to cations such as $C_6H_5(X)FeCp^+$, with $X = CH_3$, $CH_3O$, Cl or $COOCH_3$, the addition took place exclusively at the arene ring, with the hydride ion adding from the *exo* direction and with the site of addition dependent on the nature of substituent X. Recently, we have studied the product distributions in the hydride addition to 15 cyclopentadienyliron (CpFe) complexes of monosubstituted benzenes [6] and concluded that, while electronic effects played a major role, as suggested by Watts and coworkers [2–5], steric factors and possibly free valency effects favoring *o*-addition as indicated by the theoretical calculations of Clack and Kane-Maguire [7] could also exert their influence on the overall product distribution. We have also recently reported that the cyanide ion [8] or the carbanions-enolate anions derived from ketones [9] could add regiospecifically to the *o*-position of a CpFe complexed arene containing an electron-withdrawing substituent. In the present work, in order to evaluate further the possibility of steric effects on nucleophilic addition reactions, we have investigated the additions of the hydride ion, the cyanide ion and the acetonyl anion to CpFe complexed substituted benzenes with an electron-withdrawing substituent, but also hindered at the *ortho*-positions with a 2-methyl or 2,6-dimethyl groups.

## Results and discussion

The CpFe complexed substituted benzenes utilized as substrates in the nucleophilic addition reactions were $2\text{-}CH_3C_6H_4(X)FeCp^+$ $PF_6^-$, with $X = NO_2$, CN, $SO_2C_6H_4CH_3$-*p* and Cl (I, II, III and IV, respectively) and $2,6\text{-}(CH_3)_2C_6H_3$-$(X)FeCp^+$ $PF_6^-$, also with $X = NO_2$, CN, $SO_2C_6H_4CH_3$-*p* and Cl (V, VI, VII and VIII, respectively). The 2-methylnitrobenzene complex I has been prepared from the oxidation of the 2-methylaniline complex with $H_2O_2/CF_3COOH$ [10]. Similarly, the 2,6-dimethylnitrobenzene complex V was obtained from an analogous oxidation of $\eta^6$-2,6-dimethylaniline-$\eta^5$-cyclopentadienyliron hexafluorophosphate (IX), the latter complex, IX, being prepared from a ligand exchange reaction between ferrocene (FcH) and 2,6-dimethylaniline. A ligand exchange reaction between FcH and 2-methylchlorobenzene to give complex IV has been reported [3], and a similar reaction between FcH and 2,6-dimethylchlorobenzene gave complex VIII. Reaction between IV or VIII and NaCN resulted in a nucleophilic substitution to give, respectively, 2-methylcyanobenzene complex II or 2,6-dimethylcyanobenzene complex VI, analogous to a similar reaction between the cyanide ion and the chlorobenzene complex reported by Nesmeyanov and coworkers [11]. A nucleophilic substitution reaction between 2-methylnitrobenzene complex I and *p*-methylbenzenethiol gave rise to $\eta^6$-2-methyl-*p*-methylphenylthiobenzene-$\eta^5$-cyclopentadienyliron hexafluorophosphate [12] which in turn was oxidized with *m*-chloroperbenzoic acid [13] to give the 2-methyl-*p*-methylphenylsulfonylbenzene complex III. In a similar way, reaction of the 2,6-dimethylnitrobenzene complex V with *p*-methylbenzenethiol gave $\eta^6$-2,6-dimethyl-*p*-methylphenylthiobenzene-$\eta^5$-cyclopentadienyliron hexafluorophosphate (X), which was oxidized to give the 2,6-dimethyl-*p*-methylphenylsulfonylbenzene complex VII. In these preparations, new complexes II, III and V to X were obtained and the $^1H$ and $^{13}C$ NMR spectral data for these complexes are summarized in Tables 1 and 2.

Table 1

$^1$H NMR data for complexes II, III and V to X [a]

| Complex | δ(ppm from TMS) [b] | | | |
|---|---|---|---|---|
| | Cp | $CH_3$ | Complexed Ar | Others |
| II | 5.46(s,5H) | 2.82(s,3H) | 6.70–7.02(m, 4H) | – |
| III | 5.42(s,5H) | 2.74(s,3H) | 6.40–7.30(m, 4H) | 2.45(s,3H,PhC$H_3$); 7.55, 7.99(two br.s, 4H, Ph) |
| V | 5.44(s,5H) | 2.65(s,6H) | 6.59(t,*J* 6.1, 1H, H(4)); 6.68(d,*J* 6.1, 2H, H(3,5)) | – |
| VI | 5.27(s,5H) | 2.77(s,6H) | 6.57(br.s, 3H) | – |
| VII | 5.36(s,5H) | 2.83(s,6H) | 6.52(overlapping d, 2H, H(3,5)); 6.61(overlapping t, 1H, H(4)) | 2.45(s, 3H, PhC$H_3$); 7.53, 7.95(two d, *J* 7.9, 4H, Ph) |
| VIII | 5.12(s,5H) | 2.67(s,6H) | 6.24(t,*J* 6.1, 1H, H(4)); 6.48(d,*J* 6.1, 2H, H(3,5)) | – |
| IX | 4.82(s,5H) | 2.84(s,6H) | 5.82(t,*J* 5.9, 1H, H(4)); 6.10(d,*J* 5.9, 2H, H(3,5)) | 5.63(br s, 2H, $NH_2$) |
| X | 5.15(s,5H) | 2.67(s,6H) | 6.27–6.51(m,3H) | 2.28(s, 3H, PhC$H_3$); 7.13(br s, 4H, Ph) |

[a] Complexes II, III, V, VI, VII, VIII, IX and X are the hexafluorophosphate salts of 2-$CH_3C_6H_4$(CN)-$FeCp^+$, 2-$CH_3C_6H_4(SO_2PhCH_3$-*p*)$FeCp^+$, 2,6-$(CH_3)_2C_6H_3(NO_2)FeCp^+$, 2,6-$(CH_3)_2C_6H_3$(CN)Fe-$Cp^+$, 2,6-$(CH_3)_2C_6H_3(SO_2PhCH_3$-*p*)$FeCp^+$, 2,6-$(CH_3)_2C_6H_3$(Cl)$FeCp^+$, 2,6-$(CH_3)_2C_6H_3(NH_2)$-$FeCp^+$ and 2,6-$(CH_3)_2C_6H_3(SPhCH_3$-*p*)$FeCp^+$, respectively; all of these complexes gave satisfactory C, H and N analyses. [b] The solvent was acetone-$d_6$ except that $CD_3NO_2$ was used for II and VI; the *J* values are in Hz.

Reaction of I, II, III or IV as substrate with $NaBH_4$ in tetrahydrofuran (THF) [6] resulted in the *exo*-addition of the hydride ion at the C(2), C(6), C(3), C(5) and C(4) positions of the substrate giving rise to products to be designated as the *o*-2, *o*-6, *m*-3, *m*-5 and *p*-4 adducts, respectively. No *ipso*-addition at the C(1) position of the substrate was observed. As shown in Scheme 1, from complex I, for example, the

*(Continued on p. 73)*

Table 2

$^{13}$C NMR data for complexes II, III and V to X

| Complex | δ(ppm from TMS) [a] | | | |
|---|---|---|---|---|
| | Cp | $CH_3$ | Complexed Ar | Others |
| II | 78.7 | 18.0 | 73.4*, 86.3, 88.3 88.4, 88.8, 104.9* | 114.5(CN) |
| III | 80.4 | 21.6 | 88.6, 89.0, 91.5, 91.9, 103.9*, 105.6* | 19.1(Ph*C*$H_3$); 129.3, 131.5, 136.4*, 147.5*(Ph) |
| V | 80.9 | 16.5 | 87.2, 88.7, 97.4*, 124.7* | – |
| VI | 80.8 | 20.3 | 76.6*, 88.8, 89.5, 106.1* | 115.8(CN) |
| VII | 80.5 | 21.6 | 90.4, 91.8, 104.5*, 105.2* | 21.5(Ph*C*$H_3$); 128.2, 131.2, 138.2*, 147.1*(Ph) |
| VIII | 80.0 | 20.1 | 86.7, 88.6, 102.7*, 109.4* | – |
| IX | 77.3 | 22.1 | 79.8, 87.5, 104.6*, 124.0* | – |
| X | 79.4 | 21.4 | 88.1, 89.7, 100.9*, 108.1* | 20.9(Ph*C*$H_3$); 129.3, 131.2, 131.5*, 138.2*(Ph) |

[a] The solvent was acetone-$d_6$ except that $CD_3NO_2$ was used for II and VI; asterisks denote quaternary carbons.

Table 3

$^1$H NMR data for the hydride addition products of I, II, III and IV

| Adduct [b] | $\delta(CDCl_3)$ (ppm from TMS) [a] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Cp | $CH_3$ | H(1) | H(2) | H(3) | H(4) | H(5) | H(6-*endo*) | H(6-*exo*) | Others |
| Ia | 4.36 | 1.82 | – | 5.65 | 6.40 | [c] | 2.74 | – | 2.04 | – |
| | $J(2-3) = 5.4$; $J(2-4) = 0.9$; $J(4-5) = 6.4$; $J(3-5) = J(2-5) = 1.3$; $J(6-exo-CH_3) = 6.4$ | | | | | | | | | |
| Ib | 4.31 | 2.44 | – | – | 6.22 | 4.74 | 3.24 [d] | 3.26 [d] | 1.66 | – |
| | $J(3-4) = 5.0$; $J(3-5) = 0.6$; $J(6\text{-}endo\text{-}6\text{-}exo) = 11.5$; $J(5-6\text{-}exo) = 0.9$ | | | | | | | | | |
| Ic | 4.32 | 1.42 | – | – | 7.18 | [c] | [c] | [c] | [c] | – |
| | $J(3-4) = 5.2$; $J(3-5) = 1.0$ | | | | | | | | | |
| Id | 4.28 | 2.95 | 2.74 | – | – | 5.79 | [c] | [c] | 1.45 [d] | – |
| | $J(1\text{-}6\text{-}endo) = 6.4$; $J(4-5) = 6.4$; $J(1-4) = 0.8$ | | | | | | | | | |
| Ie | 4.43 | 2.20 | 3.34 | – | – | [c] | 2.34 | 2.62 | [c] | – |
| | $J(1\text{-}6\text{-}endo) = J(5\text{-}6\text{-}endo) = 6.8$; $J(6\text{-}endo\text{-}6\text{-}exo) = 12.8$ | | | | | | | | | |
| IIa | 4.40 | [c] | – | 4.78 | 6.27 | [c] | [c] | – | [c] | – |
| | $J((2-3) = J(3-4) = 4.8$ | | | | | | | | | |
| IIb | 4.35 | 2.13 | – | – | 6.20 | 4.54 | 2.68 | 2.48 | 1.55 | – |
| | $J(3-4) = 4.9$; $J(4-5) = 6.6$; $J(5\text{-}6\text{-}endo) = 6.6$; $J(6\text{-}endo\text{-}6\text{-}exo) = 12.5$ | | | | | | | | | |
| IIc | 4.46 | 1.60 | – | – | 6.37 | [c] | [c] | 2.35 | [c] | – |
| | $J(3-4) = 4.8$ | | | | | | | | | |
| IId | 4.36 | 2.76 | 2.40 [d] | – | – | 4.91 | [c] | [c] | [c] | – |
| | $J(4-5) = 5.2$ | | | | | | | | | |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| IIe | 4.37 | 1.43 | 2.24 [d] | – | – | [c] | [c] | [c] | [c] | – |
| | No $J$ could be evaluated | | | | | | | | | |
| IIIa | 4.65 | 1.42 | – | 5.35 | 6.27 | [c] | 2.54 | – | [c] | 2.44($PhCH_3$); [c](Ph) |
| | $J$(2–3);5.4; $J$(4–5) = 6.2; $J$(6-*exo*-$CH_3$) = 6.7 | | | | | | | | | |
| IIIb | 4.57 | 2.36 | – | – | 5.91 | 4.59 [d] | 2.82 [d] | 2.86 [d] | 1.08 | 2.34($PhCH_3$); 7.19, 7.55(Ph) |
| | $J$(3–4) = 5.1; $J$(6-*endo*–6-*exo*) = 11.5; $J$(2–3 of Ph) = 7.9 | | | | | | | | | |
| IIIc | 4.63 | 2.39 | – | – | 6.83 | [c] | [c] | [c] | 1.28 | 2.31($PhCH_3$); [c](Ph) |
| | $J$(3–4) = 5.1; $J$(6-*endo*–6-*exo*) = 12.2 | | | | | | | | | |
| IIId | 4.53 | 2.72 | [c] | – | – | 5.18 | [c] | [c] | 1.52 | 2.21($PhCH_3$); [c](Ph) |
| | $J$(4–5) = 6.9; $J$(6-*endo*–6-*exo*) = 12.8 | | | | | | | | | |
| IIIe | 4.55 | 2.41 | 2.97 | – | – | 4.18 | [c] | [c] | 1.38 | 2.29($PhCH_3$); [c](Ph) |
| | $J$(4–5) = 6.2; $J$(1–6-*endo*) = 6.8; $J$(6-*endo*–6-*exo*) = 12.5 | | | | | | | | | |
| IVa | 4.35 | [c] | – | 4.59 | 5.95 | [c] | [c] | – | 2.28 [d] | – |
| | $J$(2–3) = 5.0; $J$(3–4) = 5.0 | | | | | | | | | |
| IVb | 4.24 | 2.01 | – | – | 5.90 | 4.14 | 2.57 | 2.89 | 1.99 | – |
| | $J$(3–4) = 4.8; $J$(3–5) = 1.9; $J$(4–5) = 6.2; $J$(5–6-*endo*) = 6.9; $J$(6-*endo*–6-*exo*) = 12.5 | | | | | | | | | |
| IVc | 4.23 | 1.61 | – | – | 6.24 | [c] | [c] | 2.44 | 1.70 | – |
| | $J$(3–4) = 5.0; $J$(3–5) = 1.0; $J$(5–6-*endo*) = 6.6; $J$(4–6-*endo*) = 0.9; $J$(6-*endo*–6-*exo*) = 12.6 | | | | | | | | | |
| IVd | 4.21 | 2.71 | 2.17 | – | – | 4.72 | [c] | [c] | 1.42 | – |
| | $J$(4–5) = 6.6; $J$(1–6-*endo*) = 6.2; $J$(6-*endo*–6-*exo*) = 11.8 | | | | | | | | | |
| IVe | 4.24 | 1.43 | 2.10 | – | – | 4.29 | [c] | [c] | 1.58 | – |
| | $J$(4–5) = 6.3; $J$(1–4) = $J$(1–5) = 1.2; $J$(1–6-*endo*) = 6.0; $J$(6-*endo*–6-*exo*) = 12.8 | | | | | | | | | |

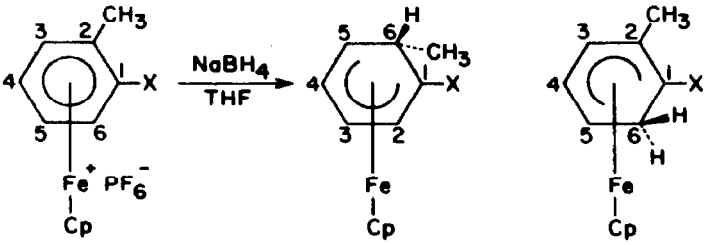
[a] $J$ values are in Hz. [b] The structure and numbering for each of these adducts are given in Scheme. 1. [c] Signals cannot be assigned due to overlapping. [d] $\delta$ values are approximate because of overlapping.

Table 4

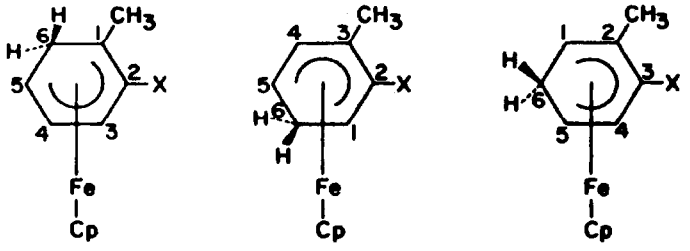
$^{13}C$ NMR data for the hydride addition products of I, II, III and IV

| Adduct | $\delta(CDCl_3)$ (ppm from TMS) [a] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Cp | $CH_3$ | C(1) | C(2) | C(3) | C(4) | C(5) | C(6) | Others |
| Ia | 74.8 | 22.2 | [b]* | 80.9 | 81.0 | 77.8 | 26.6 | 34.1 | – |
| Ib | 76.8 | 19.4 | 75.6* | 95.2* | 83.2 | 82.3 | 31.9 | 28.6 | – |
| Ic | 77.4 | 18.0 | 26.9* | [b]* | 82.8 | 77.8 | 23.0 | 42.5 | – |
| Id | 77.2 | 23.0 | 24.8 | [b]* | 91.2* | 83.0 | 24.0 | 30.2 | – |
| Ie | 77.3 | 21.2 | 26.9 | 93.8* | [b]* | 80.5 | 27.3 | 34.5 | – |
| IIa | 76.3 | 23.3 | 10.1* | 81.2 | 82.7 | 81.6 | 25.5 | 31.4 | 123.8(CN) |
| IIb | 75.9 | 20.4 | 4.1* | 95.4* | 81.7 | 81.0 | 28.0 | 24.6 | 125.7(CN) |
| IIc | 77.2 | 22.6 | 30.1* | 63.0* | 80.5 | 79.1 | 26.8 | 29.7 | 121.4(CN) |
| IId | 74.4 | 20.0 | 22.6 | 63.0* | 98.0 | 81.7 | 21.7 | 34.7 | 124.7(CN) |
| IIe | 75.4 | 20.0 | 24.7 | 96.5* | 62.8* | 81.8 | 24.5 | 33.5 | 120.9(CN) |
| IIIa | 77.2 | 28.0 | 41.2* | 78.4 | 81.5 | 79.3 | 27.7 | 32.7 | 21.5($PhCH_3$); 126.6, 128.8, 137.8*, 143.4* (Ph) |
| IIIb | 75.8 | 21.4 | 39.4* | 92.8* | 83.0 | 81.3 | 27.2 | 25.7 | 19.2($PhCH_3$); 126.3, 129.3, 139.0*, 142.5* (Ph) |
| IIIc | 76.3 | 20.2 | 34.2* | 97.4* | 82.2 | 79.9 | 22.4 | 30.2 | 17.9($PhCH_3$); 126.9, 129.4, 138.2*, 143.9(Ph) |
| IIId | 75.7 | 21.5 | 23.5 | 97.7* | 93.3* | 82.2 | 34.2 | 28.3 | 18.7($PhCH_3$); 127.6, 129.6, 140.3*, 144.2* (Ph) |
| IIIe | 76.1 | 21.5 | 25.9 | 94.1* | 97.1* | 81.9 | 24.8 | 36.5 | 20.2($PhCH_3$); 127.1, 129.5, 140.0*, 143.2* (Ph) |
| IVa | 77.2 | 21.0 | 92.9* | 78.3 | 78.4 | 77.7 | 38.0 | 36.1 | – |
| IVb | 75.9 | 20.0 | 75.2* | 89.8* | 77.9 | 77.6 | 38.0 | 27.5 | – |
| IVc | 75.8 | 19.5 | 59.2* | 105.6* | 78.0 | 76.1 | 23.0 | 34.4 | – |
| IVd | 75.8 | 22.4 | 18.9 | 105.3* | 91.5* | 78.3 | 28.5 | 33.3 | – |
| IVe | 75.3 | 20.4 | 26.2 | 89.8* | 106.7* | 79.9 | 21.5 | 30.3 | – |

[a] Asterisks denote quaternary carbons. [b] Signal not observed probably because of low intensity.



I, X = $NO_2$ Ia Ib
II, X = CN IIa IIb
III, X = $SO_2PhCH_3$-p IIIa IIIb
IV, X = Cl IVa IVb



Ic Id Ie
IIc IId IIe
IIIc IIId IIIe
IVc IVd IVe

Scheme 1

mixture of products consisted of 1–5-$\eta^5$-6-*endo*-methyl-1-nitrocyclohexadienyl-$\eta^5$-cyclopentadienyliron (Ia), 1–5-$\eta^5$-2-methyl-1-nitrocyclohexadienyl-$\eta^5$-cyclopentadienyliron (Ib), 1–5-$\eta^5$-1-methyl-2-nitrocyclohexadienyl-$\eta^5$-cyclopentadienyliron (Ic), 1–5-$\eta^5$-3-methyl-2-nitrocyclohexadienyl-$\eta^5$-cyclopentadienyliron (Id) and 1–5-$\eta^5$-2-methyl-3-nitrocyclohexadienyl-$\eta^5$-cyclopentadienyliron (Ie), respectively, as the *o*-2, *o*-6, *m*-3, *m*-5 and *p*-4 adducts.

Evidence for the presence of the various hydride addition products was deduced from high resolution 300 MHz $^1$H NMR [6,14]. As illustrated in our earlier work [6], various regions of a spectrum containing distinctly separate peaks, such as the Cp and/or $CH_3$ signals, were expanded and integrated and the ratios of the integrated areas gave the relative distribution of products in a given mixture of adducts. The $^{13}$C NMR spectrum of each mixture of adducts was also obtained using inverse gated decoupling with long delay time to give signals the integrated intensities of which could be quantitatively correlated [15,16]. From the ratios of the integrals of well separate $^{13}$C signals, the product distributions calculated were essentially in agreement with those obtained from $^1$H NMR. Data from the $^1$H and $^{13}$C NMR

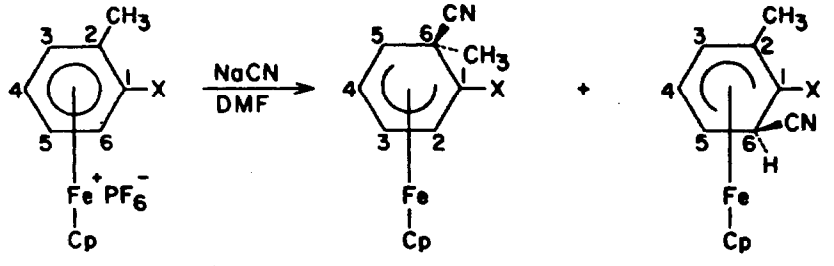
Table 5

Relative product distributions in nucleophilic additions to I, II, III and IV

| Substrate | Nucleophile | Relative distribution of adducts (%) | | | | |
|---|---|---|---|---|---|---|
| | | *o*-2 | *o*-6 | *m*-3 | *m*-5 | *p*-4 |
| I | $H^-$ | 7 | 78 | 6 | 4 | 5 |
| II | $H^-$ | 4 | 82 | 5 | 5 | 4 |
| III | $H^-$ | 4 | 81 | 6 | 3 | 6 |
| IV | $H^-$ | 6 | 56 | 15 | 9 | 14 |
| I | $CN^-$ | 2 | 98 | – | – | – |
| II | $CN^-$ | 6 | 94 | – | – | – |
| III | $CN^-$ | 4 | 96 | – | – | – |
| I | $CH_3COCH_2^-$ | – | 100 | – | – | – |
| II | $CH_3COCH_2^-$ | – | 100 | – | – | – |
| III | $CH_3COCH_2^-$ | 6 | 94 | – | – | – |
| IV | $CH_3COCH_2^-$ | – | 100 | – | – | – |

spectra for the hydride addition products of I, II, III and IV are summarized in Tables 3 and 4. For the hydride addition to each of the substrates I, II, III and IV, the relative distributions of isomeric products a, b, c, d and e would correspond to additions at the *o*-2, *o*-6, *m*-3, *m*-5 and *p*-4 positions, respectively, and these relative product distributions are given in Table 5. It may be pointed out that because a number of signals in the $^1H$ NMR spectra for the minor products from the hydride addition reactions were obscured due to overlapping (footnotes *c* and *d*, Table 3), it is possible that the designations of minor adducts as *m*-3, *m*-5 or *p*-4 in Table 5 could be changed or switched around, but this uncertainty did not detract from the finding that the major product in the hydride addition to I, II, III or IV was the *o*-6 adduct.

Reaction of substrate I, II or III with NaCN in dimethylformamide (DMF) [8], as shown in Scheme 2, resulted in the *exo*-addition of the cyanide ion to the *o*-2 and *o*-6 positions, with no *m*-3, *m*-5, *p*-4 or *ipso* adduct. A similar reaction of NaCN with IV, however, gave rise to II via a nucleophilic substitution [11], followed by cyanide addition to give IIf and IIg. Thus the same products were obtained when




I, X = $NO_2$ — If — Ig

II, X = CN — IIf — IIg

III, X = $SO_2PhCH_3$-p — IIIf — IIIg

Scheme 2

Table 6

$^1$H NMR data for the cyanide addition products of I, II and III

| Adduct [b] | δ($CDCl_3$)(ppm from TMS) [a] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Cp | $CH_3$ | H(1) | H(2) | H(3) | H(4) | H(5) | H(6-*endo*) | Others |
| If | 4.46 | 2.21 | – | 5.74 | 6.33 | [c] | 3.05 | – | – |
| | $J(2–3) = J(3–4) = 5.5$; $J(4–5) = 6.2$; $J(2–4) = J(3–5) = 1.1$ | | | | | | | | |
| Ig | 4.43 | 2.47 | – | – | 6.32 | 4.95 | 3.45 | 4.31 | – |
| | $J(3–4) = 5.2$; $J(4–5) = 6.1$; $J(5\text{-}endo) = 6.9$ | | | | | | | | |
| IIf | 4.56 | 1.97 | – | 5.13 | 6.43 | [c] | 2.70 | – | – |
| | $J(2–3) = J(3–4) = 5.3$; $J(4–5) = 6.2$; $J(2–4) = 0.8$; $J(3–5) = 1.1$ | | | | | | | | |
| IIg | 4.46 | 2.22 | – | – | 6.33 | 4.80 | 2.97 | 3.55 | – |
| | $J(3–4) = 5.4$; $J(4–5) = 6.5$; $J(5–6\text{-}endo) = 6.5$; $J(3–5) = 0.8$ | | | | | | | | |
| IIIf | 4.74 | 2.44 | – | 5.55 | 6.41 | [c] | 4.57 | – | 2.40(PhC$H_3$); c(Ph) |
| | $J(2–3) = J(3–4) = 5.5$; $J(4–5) = 5.5$; $J(2–4) = 1.1$ | | | | | | | | |
| IIIg | 4.66 | 2.35 | – | – | 6.07 | 4.80 | 3.01 | 4.00 | 2.36(PhC$H_3$); 7.27, 7.69(Ph) |
| | $J(3–4) = 5.3$; $J(4–5) = 5.8$; $J(5–6\text{-}endo) = 6.9$; $J(3–5) = 0.9$; $J(2–3$ of Ph$) = 8.3$ | | | | | | | | |

[a] $J$ values are in Hz. [b] The structure and numbering for each of these adducts are given in Scheme 2. [c] Signals cannot be assigned due to overlapping.

Table 7

$^{13}C$ NMR data for the cyanide addition products of I, II and III

| Adduct [b] | δ ($CDCl_3$) (ppm from TMS) [a] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Cp | $CH_3$ | C(1) | C(2) | C(3) | C(4) | C(5) | C(6) | Others |
| If | 76.8 | 26.0 | 68.7* | 81.8 | 81.9 | 82.4 | 35.7 | 29.4 | 119.1(CN) |
| Ig | 77.7 | 18.7 | 61.1* | 93.5* | 84.4 | 81.1 | 29.6 | 29.2 | 116.8(CN) |
| IIf | 76.5 | 24.7 | 13.4* | 80.5 | 83.7 | 81.2 | 31.9 | 32.7 | 119.6, 121.6(CN) |
| IIg | 76.9 | 20.2 | 7.1* | 94.2* | 83.6 | 79.8 | 28.4 | 23.1 | 116.9, 122.6(CN) |
| IIIg | 77.1 | 21.5 | 42.7* | 92.2* | 84.8 | 79.9 | 27.7 | 23.1 | 19.2($PhCH_3$); 117.0(CN); 127.1, 129.7, 137.8*, 144.0*(Ph) |

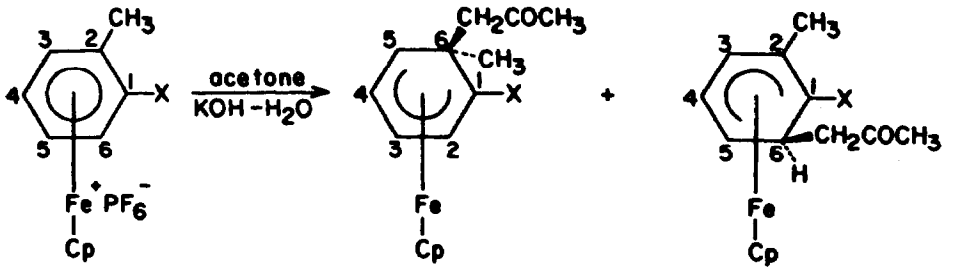
[a] Asterisks denote quaternary carbons. [b] Signals for adduct IIIf are too weak for observation.

either substrate II or IV was treated with NaCN in DMF. The $^1H$ and $^{13}C$ NMR data for these cyanide addition products are given in Tables 6 and 7, and the relative distributions of these *o*-2 and *o*-6 adducts are included in Table 5.

As reported previously [9], the reaction of I with acetone in the presence of aqueous KOH resulted in the *exo*-addition of the acetonyl anion solely at the *o*-6 position of I to give 1-5-$\eta^5$-2-methyl-1-nitro-6-*exo*-2-oxopropylcyclohexadienyl-$\eta^5$-cyclopentadienyliron (Ii). Similarly, addition of the acetonyl anion to II or IV gave only the *o*-6 adduct IIi or IVi, respectively. In the same reaction with III, however, some *o*-2 adduct IIIh, besides IIIi, was observed. These reactions are shown in Scheme 3. The $^1H$ and $^{13}C$ NMR data for the acetonyl anion addition products are summarized in Tables 8 and 9 and the relative distribution of these adducts are also included in Table 5.

In the nucleophilic addition reactions with substrates, V, VI, VII and VIII, in which both *o*-positions to the electron-withdrawing substituent were hindered by the presence of the 2,6-dimethyl groups, three products derived from additions at the *o*-, *m*- and *p*-positions of the substrate were obtained from the hydride, cyanide or acetonyl anion addition as shown in Scheme 4. For example, in the reaction of V with $NaBH_4$ in THF, products Va, Vb and Vc are the *o*-, *m*- and *p*-adducts

*(Continued on p. 82)*




| | | |
|---|---|---|
| I, X = $NO_2$ | – | Ii |
| II, X = CN | – | IIi |
| III, X = $SO_2PhCH_3$-p | IIIh | IIIi |
| IV, X = Cl | – | IVi |

Scheme 3

Table 8

$^1$H NMR data for the acetonyl anion addition products of I, II, III and IV

| Adducts [b] | δ($CDCl_3$) (ppm from TMS) [a] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Cp | $CH_3$ | H(1) | H(2) | H(3) | H(4) | H(5) | H(6-*endo*) | Others |
| Ii | 4.25 | 2.35 | – | – | 6.59 | 4.59 | 3.56 [d] | 3.55 [d] | 1.06, 1.38 ($CH_2$); 1.83 ($CH_3CO$) |
| | $J$(3–4) = 5.3; $J$(4–5) = 6.5; $J$(5–6-*endo*) = 6.5; $CH_2$: $J$(H–H) = 15.3; $J$(H–6-*endo*) = 4.3, 8.8 | | | | | | | | |
| IIi | 4.37 | 2.14 | – | – | 6.07 | 4.49 | 3.12 | 2.90 | 1.30, 1.48($CH_2$); 1.92($CH_3CO$) |
| | $J$(3–4) = 5.0; $J$(4–5) = 5.8; $J$(5–6-*endo*) = 6.5; $J$(3–5) = 0.8; $CH_2$: $J$(H–H) = 15.9; $J$(H–6-*endo*) = 5.0, 8.9 | | | | | | | | |
| IIIh | 4.56 | 2.64 | – | 5.32 | 6.21 | [c] | 2.75 | – | [c]($CH_2$); 1.76($CH_3CO$); 2.41(PhC$H_3$) 7.29, 7.78 (Ph) |
| | $J$(2–3) = $J$(3–4) = 5.3; $J$(4–5) = 6.2; $J$(2–4) = $J$(3–5) = 1.1; $J$(2–3 of Ph) = 8.3 | | | | | | | | |
| IIIi | 4.58 | 2.37 | – | – | 5.86 | 4.52 | 3.17 | 3.20 | 0.67, 0.82($CH_2$); 1.69($CH_3CO$); 2.44(PhC$H_3$) 7.32, 7.72(Ph) |
| | $J$(3–4) = 5.1; $J$(4–5) = 6.1; $CH_2$: $J$(H–H) = 15.7; $J$(H–6-*endo*) = 2.9, 10.0; $J$(2–3 of Ph) = 8.4 | | | | | | | | |
| IVi | 4.25 | 2.02 | – | – | 5.81 | 4.10 | 2.92 | 3.30 | 1.24, 1.73($CH_2$); 1.91 ($CH_3CO$) |
| | $J$(3–4) = 4.8; $J$(4–5) = 6.6; $J$(5–6-*endo*) = 6.6; $J$(3–5) = 1.1; $CH_2$: $J$(H–H) = 14.8; $J$(H–6-*endo*) = 4.4, 8.9 | | | | | | | | |

[a] $J$ values are in Hz. [b] The structure and numbering for each of these adducts are given in Scheme 3. [c] Signal cannot be assigned due to overlapping. [d] δ values are approximate because of overlapping.

Table 9

$^{13}C$ NMR data for the acetonyl anion addition products of I, II, III and IV

| Adduct | $\delta(CDCl_3)$ (ppm from TMS) [a] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Cp | $CH_3$ | C(1) | C(2) | C(3) | C(4) | C(5) | C(6) | Others |
| Ii | 76.8 | 19.4 | 65.7* | 93.1* | 83.0 | 79.9 | 38.9 | 34.9 | 29.9($CH_3CO$); 50.4($CH_2CO$); 205.9(CO) |
| IIi | 75.8 | 20.6 | 12.0* | 93.1* | 81.6 | 78.7 | 34.0 | 32.7 | 30.1($CH_3CO$); 52.6($CH_2CO$); 124.8(CN); 205.7(CO) |
| IIIh | 77.2 | 25.6 | 53.3* | 76.1 | 81.8 | 79.6 | 29.1 | 30.5* | 18.4(Ph$CH_3$); 29.9($CH_3CO$); 53.3 ($CH_2CO$); 127.0, 129.4, 140.5*, 143.3*(Ph); 206.0(CO) |
| IIIi | 76.0 | 21.3 | 46.7* | 91.2* | 83.1 | 78.4 | 31.8 | 32.2 | 19.4(Ph$CH_3$); 29.9($CH_3CO$); 50.2 ($CH_2CO$); 126.9, 129.5, 140.4*, 143.0*(Ph); 206.0(CO) |
| IVi | 75.8 | 20.1 | 65.1* | 88.0* | 78.1 | 75.5 | 34.0 | 44.1 | 30.5($CH_3CO$); 50.9($CH_2CO$); 206.9(CO) |

[a] Asterisks denote quaternary carbons.

Table 10. $^1$H NMR data for the hydride addition products of V, VI, VII and VIII

| Adduct [b] | δ($CDCl_3$) (ppm from TMS) [a] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Cp | $CH_3$ | H(1) | H(2) | H(3) | H(4) | H(5) | H(6-*endo*) | H(6-*exo*) | Others |
| Va | 4.36 | 1.51, 1.97 | – | – | 6.04 | 4.41 | 2.53 [c] | – | 2.04 | – |
| | $J$(3–4) = 5.0; $J$(4–5) = 5.8; $J$(6-*exo*–6 $CH_3$) = 6.4 | | | | | | | | | |
| Vb | 4.25 | 1.43, 2.56 | – | – | – | 4.16 | 2.13 | 2.37 | 1.67 | – |
| | $J$(4–5) = 6.4; $J$(5–6-*endo*) = 6.6; $J$(6-*endo*–6-*exo*) = 12.8 | | | | | | | | | |
| Vc | 4.19 | 1.93 | 2.12 | – | – | – | 2.12 | 2.28 | 1.52 | – |
| | $J$(1–6-*endo*) = $J$(5–6-*endo*) = 6.2; $J$(6-*endo*–6-*exo*) = 12.6 | | | | | | | | | |
| VIa | 4.35 | 1.58, 2.14 | – | – | 6.20 | 4.52 | 2.29 | – | 1.62 [c] | – |
| | $J$(3–4) = 5.0; $J$(4–5) = 6.3 | | | | | | | | | |
| VIb | 4.27 | 1.61, 2.76 | – | – | – | 4.28 | 2.28 | 2.43 | 1.56 | – |
| | $J$(4–5) = 6.0; $J$(5–6-*endo*) = 6.6; $J$(6-*endo*–6-*exo*) = 13.0 | | | | | | | | | |
| VIc | 4.21 | 2.07 | 2.28 [c] | – | – | – | 2.28 [c] | 2.45 [c] | 1.52 [c] | – |
| | No $J$ could be evaluated | | | | | | | | | |
| VIIa | 4.60 | 1.38, 2.05 | – | – | 6.02 | 4.67 | 2.40 [c] | – | 1.38 [c] | 2.35(PhC$H_3$); 7.20, 7.56(Ph) |
| | $J$(3–4) = 5.0; $J$(4–5) = 5.7; $J$(3–5) = 1.2; $J$(2–3 of Ph) = 8.0 | | | | | | | | | |
| VIIb | 4.47 | 2.39, 2.68 | – | – | – | 4.22 | 2.36 | 2.16 | 1.37 | 2.39(PhC$H_3$); 7.26, 7.72(Ph) |
| | $J$(4–5) = 6.5; $J$(5–6-*endo*) = 6.8; $J$(4–6-*endo*) = 0.8; $J$(6-*endo*–6-*exo*) = 12.6; $J$(2–3 of Ph) = 8.0 | | | | | | | | | |
| VIIc | 4.30 | 1.87 | 2.28 [c] | – | – | – | 2.28 [c] | 2.35 | 1.43 | 2.43(PhC$H_3$); 7.23, 7.96(Ph) |
| | $J$(6-*endo*–6-*exo*) = 12.0; $J$(2–3 of Ph) = 8.0 | | | | | | | | | |
| VIIIa | 4.25 | 1.60, 2.04 | – | – | 5.93 [d] | | 2.12 | – | 1.88 | – |
| | $J$(3–4) = 4.8; $J$(4–5) = 6.4; $J$(3–5) = 1.2; $J$(6-*endo*–6-*exo*-$CH_3$) = 7.0 | | | | | | | | | |
| VIIIb | 4.13 | 1.62, 2.69 | – | – | – | 4.26 | 2.02 [c] | 2.36 | 1.67 | – |
| | $J$(4–5) = 6.6; $J$(5–6-*endo*) = 6.6; $J$(4–6-*endo*) = 0.9; $J$(6-*endo*–6-*exo*) = 12.9 | | | | | | | | | |
| VIIIc | 4.11 | 2.04 | 2.06 [c] | – | – | – | 2.06 [c] | 2.23 | 1.40 | – |
| | $J$(1–6-*endo*) = $J$(5–6-*endo*) = 6.4; $J$(6-*endo*–6-*exo*) = 12.5 | | | | | | | | | |

[a] $J$ values are in Hz. [b] The structure and numbering for each of these adducts are given in Scheme 4. [c] δ values are approximate because of overlapping. [d] Signal cannot be assigned due to overlapping.

Table 11

$^{13}C$ NMR data for the hydride addition products of V, VI, VII and VIII

| Adduct | $\delta(CDCl_3)$ (ppm from TMS) [a] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Cp | $CH_3$ | C(1) | C(2) | C(3) | C(4) | C(5) | C(6) | Others |
| Va | 76.0 | 17.4, 20.0 | 78.0* | 92.1* | 80.4 | 80.0 | 41.3 [b] | 36.5 [c] | – |
| Vb | 77.5 | 17.6, 21.4 | 25.6* | 122.3* | 87.4* | 76.9 | 22.7 [b] | 34.0 [c] | – |
| Vc | 76.2 | 19.2 | 22.7 | 89.4* | 128.2* | 89.4* | 22.7 [b] | 25.7 [c] | – |
| VIa | 75.8 | 20.1, 20.6 | 12.2* | 95.5* | 82.1 | 80.4 | 32.9 | 30.4 | 124.1(CN) |
| VIb | 76.8 | 21.2, 22.2 | 31.9* | 64.1* | 94.6* | 80.0 | 23.8 | 33.5 | 120.6(CN) |
| VIc | 74.9 | 20.0 | 21.2 | 96.3* | 63.9* | 96.3* | 26.8 | 25.3 | 123.3(CN) |
| VIIa | 75.9 | 21.5, 25.4 | 34.9* | 93.9* | 84.9 | 82.1 | 26.7 | 20.5 | 21.4($PhCH_3$); 126.3, 129.3, 141.3*, 142.9*(Ph) |
| VIIb | 77.1 | 20.0, 21.0 | 42.0* | 95.1* | 92.7* | 81.2 | 34.2 | 35.5 | 21.4($PhCH_3$); 125.5, 129.5, 140.4*, 142.2*(Ph) |
| VIIc | 75.2 | 21.4 | 23.0 | 93.0* | 97.1* | 93.0* | 23.0 | 28.2 | 21.5($PhCH_3$); 127.0, 130.1, 141.8*, 143.7*(Ph) |
| VIIIa | 75.7 | 20.5, 21.1 | 66.7* | 90.0* | 78.8 | 77.2 | 35.6 | 31.9 | – |
| VIIIb | 76.5 | 19.9, 21.4 | 38.6* | 106.9* | 89.9* | 77.5 | 23.2 | 35.0 | – |
| VIIIc | 75.8 | 20.9 | 21.8 | 91.6* | 107.8* | 91.6* | 21.8 | 26.4 | – |

[a] Asterisks denote quaternary carbons. [b] $J$(C–H) values of 164.4, 162.0 and 172.4 Hz, respectively, for Va, Vb and Vc confirm the C(5) assignments as a carbon possessing some aromatic character. [c] $J$(C–H) values of 135.0, 132.7 and 135.0 Hz, respectively, for Va, Vb and Vc confirm the C(6) assignments of a carbon that is tetrahedral.

Table 12

$^1$H NMR data for the cyanide addition products of V, VI and VII

| Adduct [b] | $\delta(CDCl_3)$ (ppm from TMS) [a] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Cp | $CH_3$ | H(1) | H(2) | H(3) | H(4) | H(5) | H(6-*endo*) | Others |
| Vd | 4.53 | 1.97, 2.13 | – | – | 6.25 | 4.75 | 2.94 | – | – |
| | $J(3–4) = 5.0$; $J(4–5) = 6.2$ | | | | | | | | |
| Ve | [c] | 1.42, 2.49 | – | – | – | [c] | [c] | [c] | – |
| | No $J$ could be evaluated | | | | | | | | |
| Vf | [c] | 1.64 | [c] | – | – | – | [c] | [c] | – |
| | No $J$ could be evaluated | | | | | | | | |
| VId | 4.45 | 1.97, 2.23 | – | – | 6.35 | 4.78 | 2.66 | – | – |
| | $J(3–4) = 5.2$; $J(4–5) = 6.6$; $J(3–5) = 1.0$ | | | | | | | | |
| VIe | 4.39 | 1.43, 2.77 | – | – | – | 4.55 | 2.56 | 3.06 | – |
| | $J(4–5) = 5.1$; $J(5–6\text{-}endo) = 6.4$ | | | | | | | | |
| VIf | 4.33 | 1.57 | [c] | – | – | – | [c] | [c] | – |
| | No $J$ could be evaluated | | | | | | | | |
| VIId | 4.69 | 1.83, 2.55 | – | – | 6.20 | 4.87 | 2.55 | – | 2.37($PhCH_3$); 7.27, 7.72(Ph) |
| | $J(3–4) = 5.2$; $J(4–5) = 6.0$; $J(3–5) = 1.2$; $J(2–3$ of Ph$) = 8.3$ | | | | | | | | |
| VIIe | 4.58 | 1.96, 2.66 | – | – | – | [c] | [c] | 3.17 | 2.42($PhCH_3$); 7.31, 7.78(Ph) |
| | $J(5–6\text{-}endo = 6.6$; $J(2–3$ of Ph$) = 8.2$ | | | | | | | | |
| VIIf | 4.45 | 2.10 | [c] | – | – | – | [c] | 4.39 | 2.50($PhCH_3$); 7.52, 7.96(Ph) |
| | $J(2–3$ of Ph$) = 8.2$ | | | | | | | | |

[a] $J$ values are in Hz. [b] The structure and numbering for each of these adducts are given in Scheme 4. [c] Signals cannot be assigned due to overlapping.

Table 13

$^{13}C$ NMR data for the cyanide addition products of V, VI and VII

| Adduct [b] | δ ($CDCl_3$) (ppm from TMS) [a] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Cp | $CH_3$ | C(1) | C(2) | C(3) | C(4) | C(5) | C(6) | Others |
| Vd | 77.5 | 17.3<br>24.7 | 75.9* | 91.9* | 82.7 | 79.5 | 37.1 | 39.7* | 119.6(CN) |
| VId | 77.1 | 20.7<br>25.0 | 16.0* | 95.3* | 84.1 | 79.9 | 32.3 | 37.7* | 119.9, 121.2(CN) |
| VIId | 77.0 | 21.0<br>33.2 | 45.6* | 94.6* | 86.8 | 80.2 | 34.8 | 25.1* | 21.5($PhCH_3$); 120.0(CN);<br>126.5, 129.7, 138.7*<br>143.6*(Ph) |

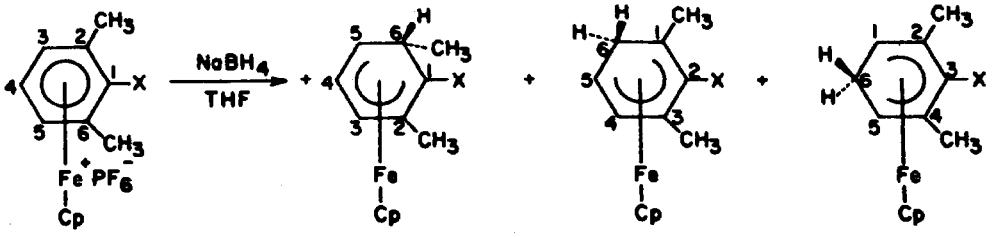
[a] Asterisks denote quaternary carbons. [b] Signals for Ve, Vf, VIe, VIf, VIIe and VIIf are too weak for observation.

obtained in this reaction. It may be noted, however, that as in the reaction of the cyanide ion with IV, treatment of VIII with NaCN in DMF proceeded by nucleophilic substitution to give VI which was followed by cyanide additions to give the same products as those obtained from a direct reaction between the cyanide ion and VI. Thus the cyanide reaction with VI or VIII gave rise to the same products VId, VIe and VIf. The $^1H$ and $^{13}C$ NMR data for the various addition products of V, VI, VII and VIII are given in Tables 10 to 15. The relative products distributions for the *o*-, *m*- and *p*-adducts obtained in the hydride, cyanide or acetonyl anion additions to V, VI, VII and VIII, with the statistical factor of 2 for the *o*- or *m*-adduct compared to the *p*-adduct taken into account, are summarized in Table 16.

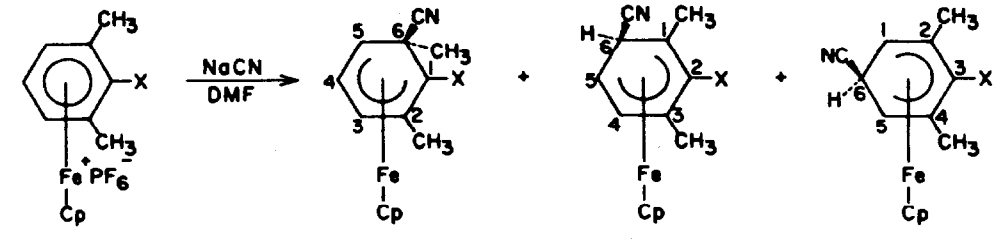
In the hydride addition to the CpFe complexed $C_6H_5X$, with X = CN, $SO_2PhCH_3$-*p* or Cl [6], the major product resulted from addition at the *o*-position, with minor amounts of *m*- and *p*-adducts also being observed. In the analogous hydride addition to the CpFe complex of 2-$CH_3C_6H_4X$, with X = CN, $SO_2PhCH_3$-*p* or Cl (II, III or IV, respectively), the major product was the *o*-6 adduct, with minor amounts of products derived from addition at the *o*-2, *m*-3, *m*-5 and *p*-4 positions (Table 5). These two sets of results from the CpFe complexed $C_6H_5X$ or 2-$CH_3C_6H_4X$ may be regarded as essentially similar, except that in the addition to II, III or IV, the chief site of reaction was the unhindered *o*-6 position rather than the *o*-2 location which was hindered by the presence of a methyl group. Similar results were obtained in the hydride addition to I, the CpFe complex of 2-$CH_3C_6H_4X$, with X = $NO_2$, the major product again being the *o*-6 adduct, with minor amounts of addition at *o*-2, *m*-3, *m*-5 and *p*-4 (Table 5). In contrast, in the hydride addition to the CpFe complexed nitrobenzene, with the highly electron-withdrawing $NO_2$ group as the only substituent, the *o*-adduct was found to be the sole product with no hydride addition at the *m*- or *p*-position [6]. It may also be pointed out that in the hydride addition to the CpFe complex of $C_6H_5N(CH_3)_2$ with the strongly electron-donating dimethylamino substituent, there was no *o*-addition and only the *m*- and *p*-adducts were obtained [6]. Apparently in the hydride addition to I, the presence of the electron-donating methyl group could have modified the electronic effect of the nitro group so that reaction could occur in all of the *o*-, *m*- and *p*-positions, with the major product derived from addition at the unhindered *o*-6 position.

Addition of the cyanide ion [8] or the acetonyl anion [9] to a CpFe complexed arene containing an electron-withdrawing substituent has been found to take place regiospecifically at the *o*-position. Similarly, the addition of the cyanide ion to I, II or III, and the addition of the acetonyl anion to I, II, III or IV, gave only *o*-addition products, with the *o*-6 adducts resulting from reaction at the unhindered site as the sole or predominant product (Table 5). It may also be pointed out that in our earlier study [8], addition of the cyanide ion to fluorenone complex XI gave a 3 : 1 mixture of adducts XIIa and XIIb, derived, respectively, from addition at C(1) and C(4a) of

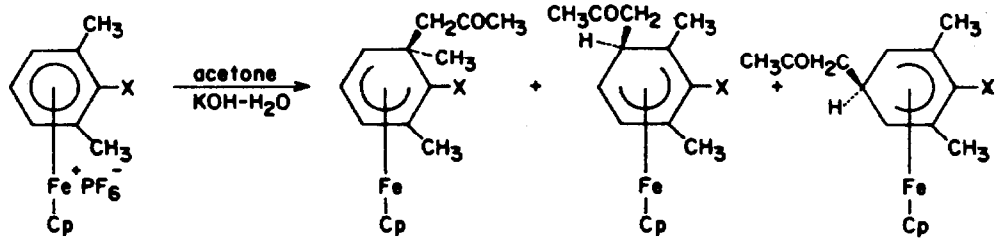
*(Continued on p. 86)*




V, X = $NO_2$ — Va, Vb, Vc
VI, X = CN — VIa, VIb, VIc
VII, X = $SO_2PhCH_3$-p — VIIa, VIIb, VIIc
VIII, X = Cl — VIIIa, VIIIb, VIIIc




V, X = $NO_2$ — Vd, Ve, Vf
VI, X = CN — VId, VIe, VIf
VII, X = $SO_2PhCH_3$-p — VIId, VIIe, VIIf




V, X = $NO_2$ — Vg, Vh, Vi
VI, X = CN — VIg, VIh, VIi
VII, X = $SO_2PhCH_3$-p — VIIg, VIIh, VIIi
VIII, X = Cl — VIIIg, VIIIh, VIIIi

Scheme 4

Table 14

$^1$H NMR data for the acetonyl anion addition products of V, VI, VII and VIII

| Adduct [b] | $\delta(CDCl_3)$ (ppm from TMS) [a] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Cp | $CH_3$ | H(1) | H(2) | H(3) | H(4) | H(5) | H(6-*endo*) | Others |
| Vg | 4.44 | 1.74, 2.05 | – | – | 6.03 | 4.47 | 3.14 | – | 1.43, 2.08($CH_2$), 1.88($CH_3CO$) |
| | $J(3–4) = 4.8$; $J(4–5) = 6.3$; $J(3–5) = 0.8$; $CH_2$: $J(H–H) = 14.8$ | | | | | | | | |
| Vh | 4.34 | 2.18, 2.58 | – | – | – | 4.18 | 2.17 | [c] | 1.18, 1.43($CH_2$); 1.93($CH_3CO$) |
| | $J(4–5) = 6.3$; $CH_2$: $J(H–H) = 1.06$; $J(H–6\text{-}endo) = 3.5, 6.0$ | | | | | | | | |
| Vi | 4.32 | 2.10 | [c] | – | – | – | [c] | [c] | [c]($CH_2$); 1.95($CH_3CO$) |
| | No $J$ could be evaluated | | | | | | | | |
| VIg | 4.37 | 1.87, 2.17 | – | – | 6.11 | 4.52 | 2.83 | – | 1.27, 1.41($CH_2$); 1.70($CH_3CO$) |
| | $J(3–4) = 5.0$; $J(4–5) = 6.5$; $J(3–5) = 0.9$; $CH_2$: $J(H–H) = 14.3$ | | | | | | | | |
| VIh | 4.29 | 1.72, 2.09 | – | – | – | [c] | [c] | [c] | [c]($CH_2$); 1.90($CH_3CO$) |
| | No $J$ could be evaluated | | | | | | | | |
| VIi | 4.23 | 2.71 | [c] | – | – | – | [c] | [c] | [c](($CH_2$); 1.86($CH_3CO$) |
| | No $J$ could be evaluated | | | | | | | | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| VIIg | 4.63 | 1.62, 2.38 | – | – | 5.99 | 4.64 | [c] | – | 0.69, 0.94($CH_2$); 1.65($CH_3CO$); 2.59(PhC$H_3$); 7.26, 7.77(Ph) |
| | $J$(3–4) = 5.1; $J$(3–5) = 1.4; $CH_2$: $J$(H–H) = 13.9; $J$(2–3 of Ph) = 8.3 | | | | | | | | |
| VIIh | 4.48 | 1.79, 2.40 | – | – | – | 4.15 | 2.50 [d] | 2.60 [d] | 0.96, 1.23($CH_2$); 1.97($CH_3CO$); 2.68(PhC$H_3$); 7.28, 7.74(Ph) |
| | $J$(4–5) = 6.2; $CH_2$: $J$(H–H) = 14.9; $J$(H–6-*endo*) = 4.2, 8.3; $J$(2–3 of Ph) = 8.3 | | | | | | | | |
| VIIi | 4.30 | 2.07 | 2.50 [d] | – | – | – | 2.50 [d] | 2.66 [d] | 1.15($CH_2$); 1.76($CH_3CO$); 2.43(PhC$H_3$); 7.33, 7.92(Ph) |
| | $CH_2$: $J$(H–6-*endo*) = 6.7; $J$(2–3 of Ph) = 8.3 | | | | | | | | |
| VIIIg | 4.26 | 2.06, 2.19 | – | – | 5.89 | [c] | 2.62 | – | 1.73($CH_2$); 1.89($CH_3CO$) |
| | $J$(3–4) = 4.4; $J$(4–5) = 6.4 | | | | | | | | |
| VIIIh | 4.23 | 2.15, 2.54 | – | – | – | 4.43 | 2.71 | [c] | 1.20, 1.57($CH_2$); 2.03($CH_3CO$) |
| | $J$(4–5) = 6.2; $CH_2$: $J$(H–H) = 10.4; $J$(H–6-*endo*) = 3.4, 6.3 | | | | | | | | |
| VIIIi | 4.21 | 2.12 | 2.88 | – | – | – | 2.88 | 2.87 | 1.27($CH_2$), 1.71($CH_3CO$) |
| | $J$(1–6-*endo*) = $J$(5–6-*endo*) = 6.1; $CH_2$: $J$(H–6-*endo*) = 7.2 | | | | | | | | |

[a] $J$ values are in Hz. [b] The structure and numbering for each of these adducts are given in Scheme 4. [c] Signals cannot be assigned due to overlapping. [d] $\delta$ values are approximate because of overlapping.

Table 15

$^{13}C$ NMR data for the acetonyl anion addition products ov V, VI, VII and VIII

| Adduct [b] | δ($CDCl_3$) (ppm from TMS) [a] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Cp | $CH_3$ | C(1) | C(2) | C(3) | C(4) | C(5) | C(6) | Others |
| Vg | 76.6 | 17.6, 25.3 | 69.3* | 90.5* | 80.8 | 78.0 | 42.6 | 46.4* | 31.7($CH_3CO$); 54.1($CH_2$); 206.6(CO) |
| Vh | 76.6 | 17.6, 25.4 | 29.3* | 122.3* | 82.0* | 80.9 | 42.7 | 46.1 | 29.2($CH_3CO$); 54.7($CH_2$); 210.9(CO) |
| Vi | 77.2 | 16.6 | 22.5 | 101.4* | 121.7* | 101.4* | 22.5 | 27.8 | 29.1($CH_3CO$); 54.6($CH_2$); 210.8(CO) |
| VIg | 76.1 | 21.0, 26.2 | 20.1* | 93.7* | 82.4 | 78.4 | 40.2 | 36.1* | 31.8($CH_3CO$); 56.4($CH_2$); 123.4(CN); 206.2(CO) |
| VIIg | 76.2 | 21.7, 22.6 | 41.1* | 92.9* | 78.8 | 77.1 | 25.8 | 30.9* | 21.4(Ph$CH_3$); 30.8($CH_3CO$); 53.7($CH_2$); 127.0, 129.4, 141.7, 143.6*(Ph), 206.5(CO) |
| VIIh | 77.1 | 23.1, 24.3 | 41.1* | 96.3* | 91.8* | 79.5 | 35.7 | 34.2 | 21.5(Ph$CH_3$); 30.1($CH_3CO$); 51.4($CH_2$); 126.6, 129.2, 140.6*, 143.2*(Ph), 206.7(CO) |
| VIIi | 75.2 | 20.5 | 28.5 | 92.8* | 99.3* | 92.8* | 28.5 | 29.1 | 21.5(Ph$CH_3$); 30.8($CH_3CO$); 55.3($CH_2$); 126.8, 129.3, 141.4*, 143.3*(Ph); 206.4(CO) |
| VIIIg | 75.6 | 18.9, 26.2 | 65.4* | 90.5* | 86.6 | 79.1 | 29.3 | 29.0 | 30.6($CH_3CO$); 55.5($CH_2$); 206.3(CO) |
| VIIIh | 76.6 | 20.4, 24.6 | 40.8* | 101.9* | 101.3* | 88.3 | 29.0 | 30.3 | 29.7($CH_3CO$); 53.1($CH_2$); 206.4(CO) |
| VIIIi | 75.9 | 20.1 | 30.1 | 108.1* | 109.5* | 108.1* | 30.1 | 24.8 | 29.3($CH_3CO$); 54.9($CH_2$); 206.4(CO) |

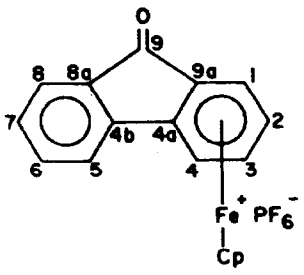
[a] Asterisks denote quaternary carbons. [b] Signals for VIh and VIi are too weak for observation.

XI, C(4a) being the more hindered quaternary C, giving rise to the minor product. A similar trend is found in the present results on cyanide addition to I, II or III, which gave the *o*-6 and *o*-2 adducts as major and minor products, respectively (Table 5).

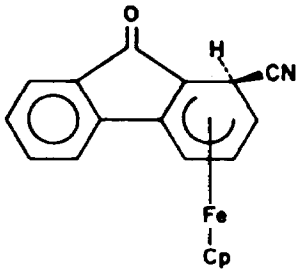
Table 16

Relative product distributions in nucleophilic additions to V, VI, VII and VIII

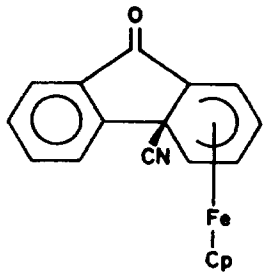
| Substrate | Nucleophile | Relative product distribution (%) | | |
|---|---|---|---|---|
| | | *o*-Adduct | *m*-Adduct | *p*-Adduct |
| V | $H^-$ | 16 | 65 | 19 |
| VI | $H^-$ | 26 | 42 | 32 |
| VII | $H^-$ | 31 | 43 | 26 |
| VIII | $H^-$ | 10 | 57 | 33 |
| V | $CN^-$ | 96 | 2 | 2 |
| VI | $CN^-$ | 93 | 4 | 3 |
| VII | $CN^-$ | 92 | 5 | 3 |
| V | $CH_3COCH_2^-$ | 88 | 8 | 4 |
| VI | $CH_3COCH_2^-$ | 90 | 6 | 4 |
| VII | $CH_3COCH_2^-$ | 78 | 16 | 6 |
| VIII | $CH_3COCH_2^-$ | 50 | 28 | 22 |




XI




XIIa




XIIb

From the above discussion, it is clear that the product distributions for the nucleophilic addition reactions with I, II, III or IV, as summarized in Table 5, all pointed to the presence of some steric hindrance by the 2-methyl substituent. Since each of these substrates contained a relatively strong electron-withdrawing substituent besides the 2-methyl group, the preferred site for nucleophilic addition was the unhindered position *ortho* to the electron-withdrawing substituent, giving rise to the *o*-6 adduct as the major product. A steric factor has also been suggested [7] as probably playing a part in accounting for the lack of *ipso*-addition in these reactions.

In studies with substrates V, VI, VII or VIII, in which both *o*-positions are hindered by the 2,6-dimethyl groups, the product distributions for the nucleophilic addition reactions as summarized in Table 16 gave further indications of a steric effect. In the hydride addition to these substrates, reaction at the *o*-positions, both of which being hindered by methyl groups, no longer gave rise to the major product. A greater proportion of *m*- and *p*-adducts were obtained, and since the *m*-positions would be closer to and more affected by the electron-withdrawing substituent than the *p*-position, the major product was the *m*-adduct, although the *o*- and *p*-adducts were also formed in significant amounts (Table 16).

In the cyanide addition to V, VI or VII, and the acetonyl anion addition to V, VI, VII or VIII, again unlike the analogous reactions with I, II, III or IV, the *o*-adduct was no longer the sole product. A similar argument may be made that since methyl groups hindered both *o*-positions, some reaction would take place at other available sites, giving rise to some *m*- and *p*-adducts besides the *o*-adduct (Table 16). If the cyanide ion and the acetonyl anion were considered to be more bulky than the hydride ion, and if steric hindrance were the most important factor, one would expect a greater proportion of *m*- and *p*-adducts to be obtained in the cyanide or acetonyl anion addition than in the hydride addition, but this was not the case (Table 16). However, the hydride addition, involving reactions with $NaBH_4$, may involve the $BH_4^-$ ion, and the tetrahedral borohydride ion [17] could be larger than a cyanide ion. On the other hand, the acetonyl anion would certainly be more bulky than the $BH_4^-$ ion as indicated by the crystallographic structure of the Janovsky adduct formed between the acetonyl anion and 1,3,5-trinitrobenzene [18,19]. Yet in both the additions of the cyanide ion and the acetonyl anion, the major product was the *o*-adduct, with much lesser proportions of *m*- and *p*-adducts than in the hydride addition. Thus factors other than steric hindrance, such as the electron-withdrawing effect of a substituent, and possibly the free valency effect suggested by the calculations of Clack and Kane-Maguire [7], both of which would favor *o*-addition,

must also play an important role in giving rise to the observed predominant formation of *o*-adducts in the cyanide ion and acetonyl anion additions to V, VI, VII or VIII.

While the present work on nucleophilic additions to CpFe complexed substituted benzenes hindered at the *o*-positions with one or two methyl groups did demonstrate the presence of a steric effect, the results also showed that, as concluded previously from studies on the hydride addition to 15 CpFe complexed monosubstituted benzenes [6], the overall product distribution is the net result of a combination of various factors, including electronic, steric and free valency effects. The nature of the substituents, which could influence the electronic and steric factors, would, of course, play its role in giving rise to the overall products. It is also clear from the present results that the nature of the nucleophile may be equally important. Different product distributions were obtained in the addition of the hydride ion, the cyanide ion or the acetonyl anion (Tables 5 and 16), and therefore, results from studies with one nucleophile, such as the hydride ion, should not be utilized for the prediction of behaviors of other nucleophiles.

## Experimental

*Preparation of substrates I to IV and V to VIII*

Substrate 2-$CH_3C_6H_4(NO_2)FeCp^+$ $PF_6^-$ (I) [10], and substrate 2-$CH_3C_6H_4(Cl)$-$FeCp^+$ $PF_6^-$ (IV) [3], are known compounds. Treatment of 0.98 g (2.5 mmol) of IV with an excess of powdered NaCN (about 1.0 g) in 12 ml of DMF with stirring for 24 h at room temperature gave 0.62 g (65%) of II, 2-$CH_3C_6H_4(CN)FeCp^+$ $PF_6^-$, as a yellow powder. Oxidation of the known 2-$CH_3C_6H_4(SPhCH_3$-*p*)$FeCp^+$ $PF_6^-$ [12] with an excess (3–5 molar equivalents) of *m*-chloroperbenzoic acid using a procedure as previously described [13] gave a 75% yield of 2-$CH_3C_6H_4(SO_2PhCH_3$-*p*)$FeCp^+$ $PF_6^-$ (III).

A ligand exchange reaction between ferrocene (FcH) and 2,6-dimethylaniline, using the same procedure as previously described for ligand exchanges between FcH and *o*-, *m*- or *p*-toluidine [20], gave a 42% yield of 2,6-$(CH_3)_2C_6H_3(NH_2)FeCp^+$ $PF_6^-$ (IX), and oxidation of this latter complex IX with $H_2O_2/CF_3COOH$ as in the reported preparation of I [10] gave substrate V, 2,6-$(CH_3)_2C_6H_3(NO_2)FeCp^+$ $PF_6^-$, in 36% yield. Reaction of V with *p*-$CH_3PhSH$ in THF in the presence of $K_2CO$, as in the analogous reaction of *p*-$CH_3PhSH$ with I [12], gave a 75% yield of 2,6-$(CH_3)_2C_6H_3(SPhCH_3$-*p*)$FeCp^+$ $PF_6^-$ (X). Oxidation of X with *m*-chloroperbenzoic acid [13], as in the preparation of III, gave a mixture of 2,6-$(CH_3)_2C_6H_3(SO_2Ph$-$CH_3$-*p*)$FeCp^+$ $PF_6^-$ (VII) and some unreacted X. After recrystallization in acetone/ether, pure VII was recovered as yellow crystals in 57% yield. A ligand exchange reaction between FcH and 2,6-dimethylchlorobenzene, as in the analogous ligand exchange with 2-methylchlorobenzene [3], gave a 32% yield of substrate VIII, 2,6-$(CH_3)_2C_6H_3(Cl)FeCp^+$ $PF_6^-$. Reaction of VIII with powdered NaCN in DMF, as in the analogous preparation of II from IV, gave a 44% yield of substrate, 2,6-$(CH_3)_2C_6H_3(CN)FeCp^+$ $PF_6^-$ (VI).

*Hydride addition reactions*

In a typical experiment, a solution of 265 mg (0.50 mmol) of 2,6-$(CH_3)_2C_6H_3(SO_2PhCH_3$-*p*)$FeCp^+$ $PF_6^-$ (VII) and 150 mg (4.0 mmol) of $NaBH_4$ in

10 ml of THF was stirred at room temperature for 0.5 h. The resulting material was filtered through a sintered glass filter and the filtrate was extracted with $CHCl_3$ ($3 \times 25$ ml). The combined extract was washed with $H_2O$, dried over $MgSO_4$, and the solvent was removed by a rotary evaporator. The residue was purified by passage through a short column (5 cm) packed with F-20 alumina (Alcoa Chemical Co.) which had been deactivated by exposure to air for 48 h. Any impurities that might be present were first removed by elution with n-pentane and then the hydride addition products were eluted with $CHCl_3$. Upon removal of the $CHCl_3$ from the eluate, 96 mg (50%) of a mixture of *o*-, *m*- and *p*-adducts VIIa, VIIb and VIIc was obtained as a dark red solid.

A similar procedure was employed in the hydride addition to 0.50–1.0 mmol of each of the other substrates. The mixture of adducts from hydride addition to I, II, III, IV, V, VI or VIII was obtained either as a red oil or a dark red solid in yields of 73, 71, 67, 66, 76, 62 or 57%, respectively.

*Cyanide addition reactions*

In a typical experiment, a mixture of 265 mg (0.50 mmol) of VII and 300 mg (6.1 mmol) of powdered NaCN in 5.0 ml of DMF was stirred at room temperature for 0.5 h. The resulting material was filtered through a sintered glass filter and the filtrate added to 150 ml of ether. The ether solution was washed thoroughly with $H_2O$ ($5 \times 60$ ml) to remove the DMF. After drying over $MgSO_4$, the ether was removed by a rotary evaporator. The residual crude product was redissolved in ether, filtered, and ether again removed to give 116 mg (57%) of a mixture of *o*-, *m*- and *p*-adducts VIId, VIIe and VIIf.

In a similar way, cyanide addition to 0.50–1.0 mmol of I, II, III, V or VI gave the corresponding mixture of adducts in yields of 76, 59, 56, 50 or 53%, respectively.

In the reaction of NaCN with IV or VIII, a substitution first took place to give II or VI, respectively, followed by cyanide addition to give the same product mixture derived directly from II or VI. The same product mixtures were obtained even when the reaction time between NaCN and IV or VIII was decreased from 0.5 h to 5 min.

*Acetonyl anion addition reactions*

In a typical experiment, a solution of 530 mg (1.0 mmol) of VII in 10 ml of acetone and 5 ml of a 20% KOH solution in $H_2O$ was stirred at room temperature for 0.5 h. About one-half of the acetone was then removed by a rotary evaporator and the remaining material was extracted with $CHCl_3$ ($3 \times 50$ ml). The combined extract was washed with $H_2O$, dried over $MgSO_4$ and the solvent removed by a rotary evaporator. The residue was redissolved in ether, filtered, and the ether removed to give 180 mg (41%) of a mixture of adducts VIIg, VIIh and VIIi as a red oil.

The same procedure was used in the addition of the acetonyl anion to I, II, III, V or VI. For the acetonyl anion addition to IV or VIII, however, a more concentrated KOH solution (50% instead of 20%) had to be employed in the initial reaction mixture. The yield of the mixture of acetonyl anion adducts from I, II, III, IV, V, VI or VIII, respectively, was 60, 52, 65, 50, 50, 48 or 31%.

**Acknowledgment**

The financial support given by the Natural Sciences and Engineering Research Council of Canada is sincerely acknowledged.

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