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Preliminary communication

THE STERIC COURSE OF PROTON ELIMINATION IN CONVERSION OF A TRICARBONYLCYCLOHEXADIENEIRON CARBINOL INTO AN ENDOCYCLIC CATION

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Summary

Tricarbonyl-1-carbomethoxy-5α^{2}*H*-cyclohexadieneiron (3) reacts with MeLi to tricarbonyl-1(1^1-hydroxy-1^1-methyl-ethyl)-5α^{2}*H*-cyclohexadieneiron (1) which yields with acid the salt tricarbonyl-1(1^1-methyl-ethyl)-5^2*H*-cyclohexadienyliron(+)-PF_6(—) (4). Retention of ^{2}H demonstrates the stereochemistry of the elimination of the ring proton as β-(*endo*).

Carbinols of type 1 with others capable of producing readily adjacent carbonium ions, are known [1,2] to be converted by HBF_4 into salts involving cations of type 4. The steric course of movement of the cationic charge on to the endocyclic complex has been shown to involve loss of a 5β-(*endo*) proton by full retention of ^{2}H in the conversion of 1 (R = ^{2}H) into 4 (R = ^{2}H).

Attachment of a complexed metal atom laterally to one face of an unsaturated molecule, such as the ring in a cyclohexa-1,3-diene, distinguishes in reactivity between the two faces [3]. Reagents attack either β-(*endo*) or α-(*exo*) according to the mechanism. The electrophilic proton attacks on the β-face, and also must be stereospecifically lost from that face during migrations of the complex around the ring, in order to explain the fully specific deuteration results [4,5]. Whether this involves a protonated Fe intermediates is not certain, but probable.

The conversion of 1 through a side-chain cation into 4 must involve loss of a proton at some stage; whether or not this occurs via a triene [6], is immaterial for the present purpose, which is to examine the stereospecificity of proton loss.

The required carbinol 1 (R = ^{2}H) was obtained in the following stages. Reduction of the known cation 2 (R = H) with borodeuteride (>95% ^{2}H) gave 3,

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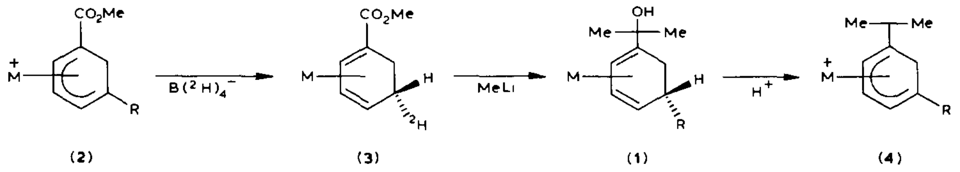
in which the situation of the ^{2}H was confirmed by ^{1}H NMR using double resonance. It accords with the normal position of attack in this cation. Because of some dubiety about the total stereospecificity of borodeuteride attack in some cases, the product **3** was subjected to attack Ph_3C^+, known to occur specifically α-(*exo*) to regenerate the deuterium-free starting cation **2** (R = H). The ester **3** reacted with MeLi (3 moles to avoid some ketone production) to form the carbinol **1** (R = ^{2}H) (>95% ^{2}H by MS). The structure was supported by ^{1}H NMR using double resonance, and exchange of OH by ^2H_2O. Consistent with previous observations it gave with HBF_4 the fluoroborate salt of the cation **4** (R = ^{2}H). The ^{1}H NMR spectra support the loss of H only. A resonance at δ 4.18 ppm due to H(5) in the cation **4** (R = H) is absent, and the presence of ^{2}H(5) was evident from the multiplicities of the resonances at δ 5.85 (d, *J* 5 Hz, H(4)) and 2.92 ppm (d, *J* 16 Hz, H(6β)).

This method, and an analogous one involving 5α-(1′-hydroxyalkyl) complexes represents a useful synthetic procedure for 1-alkyl cations with other substituents, and results will be reported elsewhere.



(2) (3) (1) (4)

(M = Fe(CO)$_3$)

Experimental

Tricarbonyl[η^4-1-(1^1-hydroxyisopropyl)5α-deuteriocyclohexa-1,3-diene] iron

The procedure below is a general one for treatment of 1-CO_2Me complexes with organometallic reagents such as MeLi or MegBr.

Tricarbonyl(η^5-1-methoxycarbonylcyclohexadienyl)iron hexafluorophosphate (1.0 g 2.37 mmol) was added to a suspension of $NaBD_4$ (126 mg, 3.0 mmol, ^{2}H > 95%, Merck) in MeCN (30 ml) at 0°C, with stirring for 1 h. Water and light petroleum were added, the petroleum extract dried and concentrated to yield a viscous oil (574 mg, 87%), identified as tricarbonyl(η^4-methoxycarbonyl-5α[^{2}*H*]-cyclohexa-1,3-diene)iron, ν_{max} 2060, 1990, 1700 cm^{-1} δ($CDCl_3$) 6.05 (H_1, 1d, $J_{2,3}$ 4 Hz, H(2)); 5.35 (H_1, dd, $J_{3,4}$ 6.5—7.0 Hz, H(3)); 3.68 (H_3, s, CO_2Me); 3.34 (H_1, ddd, $J_{4,5}$ 3.5 Hz, 1.5 Hz, H(4)); 2.19 (H_1, dd, $J_{6\alpha,6\beta}$ 14.5 Hz, $J_{5,6\beta}$ 12.0 Hz, H(6β)); 1.88 (H_1, dm, H(5)); 1.4 ppm (H_1, dm, H(6α); *m/z* 279 (*M*); 251 (*M* — CO); 223 (*M* — 2CO); 197 (*M* — 3CO); Calculated ^{2}H >95%-*d*.

This ester (500 mg, 1.8 mmol) in CH_2Cl_2 (20 ml) was cooled to —78°C and MeLi (1.4 *M* solution in ether, 3.85 ml) added. After 2 h reaction with MeLi, addition to water and extraction with CH_2Cl_2, followed by crystallisation from light petroleum gave tricarbonyl[η^4-1-(1^1-hydroxyisopropyl)-5α[^{2}*H*]-cyclohexa-1,3-diene] iron (418 mg, 82%) m.p. 62—63.5°C, ν_{max} ($CHCl_3$) 3550, 2040, 1970 cm^{-1}; δ($CDCl_3$) 5.69 (H_1, s, $J_{2,3}$ 4.5—5.0 Hz, H(2)); 5.16

(H$_1$, dd, $J_{3,4}$ 6.0 Hz, H(3)); 3.04 (H$_1$, ddd, $J_{4,5}$ 2.5 Hz, J 1 Hz, H(4)); 1.82—1.45 (H$_3$, m, H(5), 2H(6)); 1.47 (H$_3$, s, Me); 1.37 (H$_3$, s, Me) 1.30 ppm (H$_1$, s, D$_2$O exchange, OH); *m/z* 279 (*M*); 251 (*M* − CO); 233 (*M* − CO − H$_2$O); 223 (*M* − 2CO) ; 197 (*M* − 3CO); Calculated ^{2}H >95%-d_1.

Tricarbonyl[η^5-1-isopropyl-5[^2H]-cyclohexadienyl] iron hexafluorophosphate

The carbonyl above (150 mg 0.54 mmol) in propionic anhydride (0.2 ml) was treated with HBF$_4$-etherate (0.5 ml) at 0°C for 30 min. Addition of ether/light petroleum (2/1) gave a yellow precipitate, washed several times with the same mixture. To a solution in the minimum of water was added NH$_4$PF$_6$, the precipitate being dried, dissolved, in nitromethane, and precipitated by ether/light petroleum (2/1). The yellow solid (80%) was tricarbonyl(η^5-1-isopropyl-5[^{2}*H*]-cyclohexadienyliron hexafluorophosphate, ν_{max} 2120, 2080 cm^{-1} ; δ (CD$_3$CN) 6.98 (H$_1$, t, J 5—6 Hz, H(3)); 5.85 (H$_1$, d, $J_{3,4}$ 5 Hz, H(4)); 5.48 (H$_1$, d, $J_{2,3}$ 6 Hz, H(2)); 2.92 (H$_1$, d, $J_{6\alpha,6\beta}$ 16 Hz, H(6β)) 2.4—2.1 (H$_2$, m, H(6α) and C*H*Me$_2$); 1.08, 0.96 ppm (H$_3$, H$_3$, d,d J 7 Hz, CH*Me*$_2$). By contrast, the undeuterated salt showed: δ (CD$_3$CN) 6.98 (H$_1$, t, J 5—6 Hz, H(3)) 5.85 (H$_1$, t, J 5—6 Hz, H(4)); 5.48 (H$_1$, d, J 6 Hz, H(2)); 4.18 (H$_1$, t of m, $J_{4,5}$ = $J_{5,6\beta}$ = 6 Hz, J = 1 Hz, H(5)); 2.92 (H$_1$, d,d $J_{6\alpha,6\beta}$ 16 Hz, H(6β)); 2.4—2.1 (H$_2$, m, H(6β) and C*H*Me$_2$); 1.08; 0.96 ppm (H$_3$, H$_3$, d,d J 7 Hz CH*Me*$_2$).

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