Tetrahedron Letters Vol. 21, pp 1995 - 1996

0040-4039/80/0502-1995$02.00/0

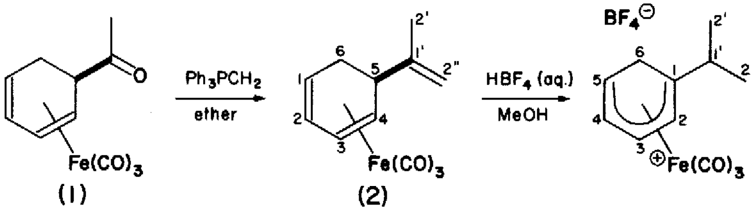
PROTONATION AND ACETYLATION OF TRICARBONYL-5-EXO-(ISOPROPENYL)CYCLOHEXA-1,3-DIENEIRON. REGIOSPECIFIC FORMATION OF TRICARBONYL-1-(SUBSTITUTED)CYCLOHEXADIENYLIUMIRON CATIONS

Brian F.G. Johnson, Jack Lewis,* G. Richard Stephenson+
University Chemical Laboratories, Lensfield Road, Cambridge, CB2 1EW

SUMMARY: *Tricarbonyl-5-exo-(isopropenyl)cyclohexa-1,3-dieneiron was prepared by means of the Wittig reaction. Protonation and acetylation of this complex resulted in the regiospecific formation of tricarbonyl-1-(substituted)cyclohexadienyliumiron cations, by hydrogen transfer from the ring to the side-chain.*

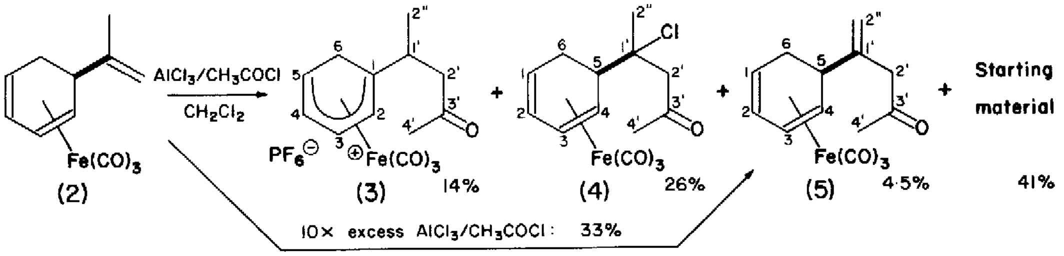
Preparation of iron stabilised cations by protonation of tricarbonyliron complexes of conjugated trienes is a common procedure, particularly for acyclic systems[1] and large rings.[2] We describe here a simple, regiospecific formation of tricarbonyl-1-(substituted) cyclohexadienyliumiron cations by electrophillic attack at an olefinic side-chain, separated from the conjugated diene by an sp^3 centre. Hydrogen transfer from the ring to the side-chain occurs to give a metal stabilised dienylium cation as the final product.

Tricarbonyl-5-exo-(acetyl)cyclohexa-1,3-dieneiron (1) is obtained from tricarbonylcyclohexadienyliumiron tetrafluoroborate by addition of $^-$CN and treatment of the product with methylmagnesium iodide.[3] Reaction of (1) with methylenetriphenylphosphoniumylide in ether afforded tricarbonyl-5-exo-(isopropenyl)cyclohexa-1,3-dieneiron (2) in 71% yield. (IR: 2046, 1977, 1973 cm^{-1} (cyclohexane); PMR: (ppm, δ) 1.23 exo H6, 1.42 endo H6, 1.54 H2' (Me singlet), 2.12 endo H5, 2.93 H1 and H4, 4.62 H2" (methylene doublet), 5.30 H2 and H3 ($CDCl_3$); CMR: 19.4 C2', 29.5 C6, 46.2 C5, 60.2 C1, 64.8 C4, 85.1 C2 and C3, 110.3 C2", 148.9 C1' (low intensity), 211.8 M-CO ($CDCl_3$); Calc. for $C_{12}H_{12}O_3Fe$: C 56.4%, H 5.0%; Found: C 55.4%, H 4.65%; *m/e* M^+ (260) -3CO -H_2). Protonation with HBF_4 (aq) in methanol, partial removal of solvent and precipitation of the product with ether gave tricarbonyl-1-(isopropyl)cyclohexadienyliumiron tetrafluoroborate.[4] Slow addition of FSO_3H to (2) in liquid sulphurdioxide at -78° was performed in an NMR tube. The CMR spectrum was that of the rearrangement product (17.8 C2", 19.2 C2', 27.1 C6, 34.7 C1', 61.0 C5, 85.3 C3, 94.5 C4, 99.5 C2, 100.8 C1 (singlet in gyrogated spectrum)). No intermediates could be detected,



+Present address: Research School of Chemistry, Australian National University, P.O. Box 4, Canberra, A.C.T. 2600, Australia though initial protonation is presumed to occur at the uncoordinated olefin forming a tertiary carbonium ion at Cl'.

Acetylation of (2) was also examined. Treatment with fused acetyl chloride/aluminium trichloride (1 equiv., 1:1 mixture) in CH_2Cl_2 at -78° gave tricarbonyl-1-(1-methyl-3-oxo-butyl)cyclohexadienyliumiron hexafluorophosphate (3) in 14% yield. The cationic product was isolated by addition of water and extraction with ether. Saturated NH_4PF_6 (aq) was added to the aqueous phaze, which was then extracted with CH_2Cl_2. The yellow extract was evaporated to give (3) as a pale yellow powder. (IR: 2107, 2056, 1964 cm^{-1} (CH_3CN); PMR: (ppm, δ) 1.01 H2" (Me doublet), 1.90 H4' (Me singlet) 2.10 exo H6, 2.35 H2', 2.80 endo H6, 4.20 H5, 5.52 H2, 5.93 H4, 7.02 H3 (H1' obscured), (CH_3CN); Calc. for $C_{14}H_{15}F_6O_4PFe$: C 37.1%, H 3.40%; Found: C 37.5%, H 3.37%. Starting material (41%) was recovered from the combined ether fractions by chromatography (silica/hexane). Further elution of the column (1:1 hexane/ether) gave two additional products which were separated by preparative TLC (silica/benzene): tricarbonyl-5-exo-(1-methyl-1-chloro-3-oxo-butyl)cyclohexa-1,3-dieneiron (4), (26%); (IR: 2048, 1979, 1974 cm^{-1} (cyclohexane); PMR: (ppm, δ) 1.10 exo H6, 1.55 H2" (Me singlet), 2.00 endo H6, 2.20 H4' (Me singlet), 2.50 endo H5, 2.70 and 2.85 H2' (2 singlets) 3.05 H1 and H4, 5.32 H2 and H3 ($CDCl_3$); Calc. for $C_{13}H_{15}ClO_4Fe$: C 49.7%, H 4.51%; *m/e* M^+ (340, 338) -3CO, -HCl, $-H_2$) and tricarbonyl-exo-(1-methylene-3-oxo-butyl) cyclohexa-1,3-dieneiron (5), (4.5%); (IR: 2048, 1977 cm^{-1} (cyclohexane); PMR: (ppm, δ) 1.30 exo H6, 1.45 endo H6, 2.00 endo H5, 2.17 H4' (Me singlet), 2.38 H2' (methylene singlet) 3.00 H1 and H4, 4.95 H2" (methylene doublet), 5.43 H2 and H3 ($CDCl_3$); Calc. for $C_{14}H_{14}O_4Fe$: C 57.0%, H 5.15%; Found: C 55.7%, H 4.67%; *m/e* M^+ (302) -3CO, $-H_2$). When acetylation was performed with a 10 fold excess of the Perrier complex, no cationic products were obtained and only tricarbonyl-5-exo-(1-methylene-3-oxo-butyl)cyclohexa-1,3-dieneiron (5), (33%) was isolated from the ether extracts.



References

1. B.F.G. Johnson, J. Lewis, D.G. Parker, S.R. Postle, *J.C.S. Dalton*, 794 (1977).
2. D. Cunningham, P. McArdle, H. Sherlock, B.F.G. Johnson, J. Lewis, *J.C.S. Dalton*, 2340 (1977); M. Brookhart, K.J. Karel, L.E. Nance, *J. Organometallic Chem.*, 203, 140 (1977).
3. B.F.G. Johnson, J. Lewis, D.G. Parker, *J. Organometallic Chem.*, 314, 141 (1977); B.F.G. Johnson, J. Lewis, D.G. Parker, P.R. Raithby, G.M. Sheldrick, *J. Organometallic Chem.*, 115, 150 (1978).
4. This salt has also been prepared by protonation of tricarbonyl-1-(2-hydroxyisopropyl) cyclohexa-1,3-dieneiron. C.R. Jablonski, T.S. Sorensen, *Canadian J. Chem.*, 2085, 52 (1974).

(Received in UK 29 February 1980)