An Approach to Regio- and Stereo-controlled Synthesis of 5,6-Disubstituted Cyclohexadiene Derivatives *via* Tricarbonyl[1—5-η-6-*exo*-(2-acetoxypropyl)cyclohexadienylium]iron Tetrafluoroborate[1]

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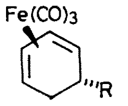
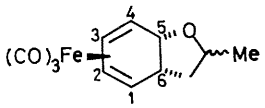
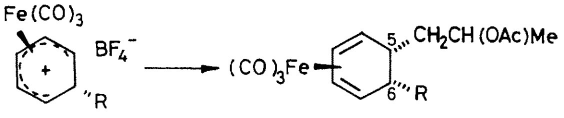
Summary The title complex (**3**) has been prepared by a route involving oxidative cyclisation of (**2**) by thallium(III) trifluoroacetate; reaction of (**3**) with nucleophiles is regiospecific, stereospecific, and diastereoselective.



(**1**)a, R = H
b, R = CH_2COMe
c, R = $CH_2CH(OH)Me$



(**2**)



(**3**)R = $CH_2CH(OAc)Me$

(**4**)a, R = $CH(CO_2Me)_2$
b, R = SPh

Intrigued by the possibility of regio- and stereo-controlled addition of nucleophiles, we wished to obtain a tricarbonylcyclohexadienyliumiron salt with a 6-*exo* substituent on the dienylium ligand (**3**, R ≠ H). Such a complex is inaccessible by the normal route, *viz.*, hydride abstraction from (**1**, R ≠ H) using triphenylmethylium tetrafluoroborate, owing to steric factors.[2] Consequently, an alternative method is required, and in this context we noted the oxidative cyclisation of enolic ester groups on to a diene–$Fe(CO)_3$ group using manganese dioxide, reported by Birch,[3] and the reaction of (**1a**) with thallium(III) trifluoroacetate in ethanol to give moderate yields of (**1**, R = OEt), reported by Lewis.[4] An intramolecular equivalent of the latter reaction might well provide an entry into the desired compounds, and we now disclose the results of our preliminary investigations in this area.

Reduction of the ketone (**1b**)[2] with sodium borohydride gave the diastereoisomeric alcohols (**1c**) quantitatively as a gold syrup.† Oxidative cyclisation was achieved by treatment of this compound (ethanol, −10 °C, N_2 atmosphere) with thallium(III) trifluoroacetate (1·2 equiv.) for 5 min, followed by sodium hydrogen carbonate (3 equiv., neutralises acid generated). Addition of ether, filtration through basic alumina, and removal of volatile material *in vacuo*, followed by chromatography afforded, in 84% yield, the complex (**2**) as an oil mainly consisting of (75—80%) a single diastereoisomer (n.m.r.).‡ Spectral data† were consistent with this structure and particularly noteworthy is the H-5 signal (δ 4·54) showing coupling (9 Hz) between H-5 and H-6, consistent with a dihedral angle of *ca.* 0—10° shown by available *X*-ray data,[5] and the smaller coupling (3·5 Hz)

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† All new compounds were characterised by n.m.r. and i.r. spectroscopy and gave satisfactory analytical and/or high resolution mass spectral data. Full details will be given elsewhere. All compounds were obtained as enantiomeric mixtures.

‡ Without addition of $NaHCO_3$ the yield is *ca.* 40% suggesting partial opening of the oxygen ring in (**2**). The diastereoisomeric excess observed undoubtedly results from re-closure in a preferred fashion on addition of base.

between H-4 and H-5, comparable with terminal diene and *endo*-protons of other complexes.[2,3] Treatment of (**2**) in acetic anhydride (0 °C) with tetrafluoroboric acid (1·2 equiv., 15 min), followed by precipitation with ether gave the desired salt (**3**) as a pale yellow microcrystalline solid in 92% yield. The structure was readily confirmed from its ^{1}H n.m.r. spectrum, showing all the expected signals associated with the dienyl protons,[2] and the expected symmetrical structure.

Reaction of (**3**) with dimethyl sodiomalonate[6] gave the expected product (**4a**), which was mainly (75—80%) a single diastereoisomer§ (n.m.r.), but in rather disappointing yield (45—50%). Isolation of an unstable second component (*ca.* 15%) indicated that some addition of nucleophile to CO ligand had occurred, as with some ruthenium complexes[7] (i.r. 2080, 2020, 1750, 1738, and 1690 cm^{-1}), but we were unable to obtain satisfactory n.m.r. data to establish its structure conclusively. Whilst we were fairly confident that the stereochemistry of (**4a**) was as shown, we were unable to establish this from inspection of the H-6 n.m.r. signal owing to the presence of overlapping resonances. Consequently (**3**) was converted into (**4b**) (PhSH, Et_3N, tetrahydrofuran, 94% yield), again mainly as one diastereoisomer.§ Recrystallisation from pentane afforded a single isomer, m.p. 77—78 °C, which now showed H-6 as a doublet of doublets at the easily observed shift of δ 3·78. The coupling constants exhibited by H-5 ($J_{4,5}$ 3 Hz and $J_{5,6}$ 9·5 Hz) were comparable with those of (**2**), which demonstrates convincingly that the phenylthio and 2-acetoxypropyl groups are *cis*. There is no reason to believe, from the available literature, that carbon and other nucleophiles behave differently in their reactions with these complexes.¶

In summary, the complex (**3**) undergoes regiospecific, stereospecific, and diastereoselective reaction with nucleophiles by chirality transfer.

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§ This can be explained by consideration of the preferred conformation of the $CH_2CH(OAc)Me$ substituent in (**3**), and will be discussed more fully elsewhere.

¶ However, it is known that some conversion of *exo*-MeO into *endo*-MeO occurs under forcing conditions: K. E. Hine, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Chem. Commun.*, 1975, 81.

[1] For previous paper (Part 7) in the series, 'Organoiron Complexes in Organic Synthesis,' see A. J. Pearson, E. Mincione, M. Chandler, and P. Raithby, *J. Chem. Soc., Perkin Trans.* 1, in the press.

[2] A. J. Birch, K. B. Chamberlain, M. A. Haas, and D. J. Thompson, *J. Chem. Soc., Perkin Trans.* 1, 1973, 1882.

[3] A. J. Birch, K. B. Chamberlain, and D. J. Thompson, *J. Chem. Soc., Perkin Trans.* 1, 1973, 1900.

[4] B. F. G. Johnson, J. Lewis, and D. G. Parker, *J. Organomet. Chem.*, 1977, **127**, C37.

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[7] R. J. H. Cowles, B. F. G. Johnson, P. L. Josty, and J. Lewis, *Chem. Commun.*, 1969, 392.