Tetrahedron Letters,Vol.25,No.4,pp 387-390,1984
Printed in Great Britain

0040-4039/84 $3.00 + .00

REGIO- AND STEREOCONTROLLED FUNCTIONALIZATION OF THE SEVEN-MEMBERED RING USING ORGANOMANGANESE CHEMISTRY

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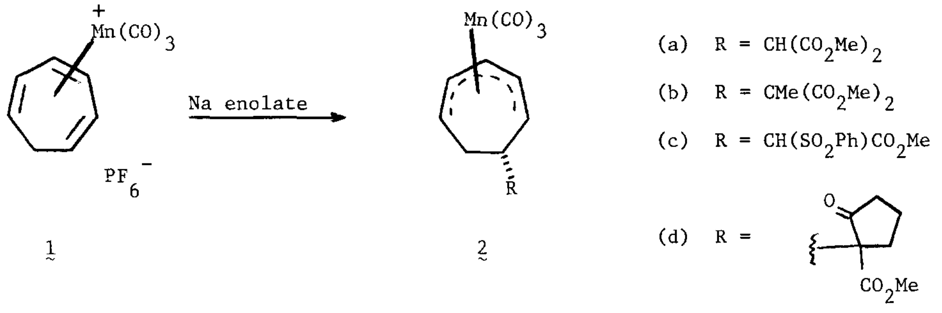
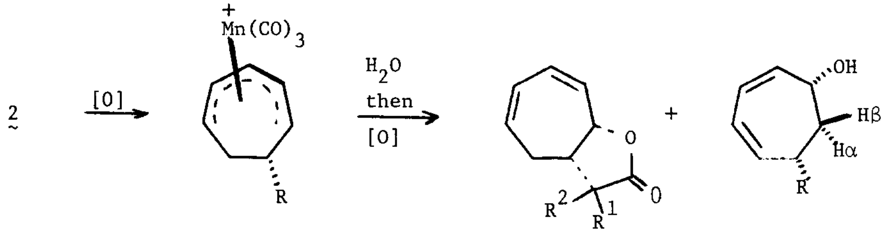
Abstract Reaction of enolate nucleophiles with cycloheptatriene-Mn$(CO)_3$ hexafluorophosphate gives substituted cycloheptadienyl-Mn$(CO)_3$ complexes, which can be decomplexed with concomitant oxygenation of the cycloheptane ring either by direct cerium(IV) oxidation or by a novel cycloetherification procedure.

A major problem which attends any projected application of triene-Mn$(CO)_3$ cationic complexes to organic synthesis is further manipulation of the neutral dienyl-Mn$(CO)_3$ species which result from their reactions with nucleophiles. Whilst it has been reported that the cyclohexadienyl complexes obtained from arene-Mn$(CO)_3$ complexes may be activated toward further nucleophile addition by replacing one CO ligand with NO^+, we envisage that this procedure may be limited to complexes which do not contain sensitive functional groups.[1] Similar activation of π-allyl-Mo$(CO)_2$Cp complexes has been reported by Faller's group.[2] For both of these types of complex there is a need to develop direct methods of ligand disengagement with concomitant introduction of extra functionality, and we report herein two potentially general methods for such a transformation.



Cycloheptatriene-Mn$(CO)_3$ hexafluorophosphate[3] 1 was found to react with a range of enolate nucleophiles to give dienyl complexes 2 in which the presence of sensitive functional groups prevented activation by CO/NO^+ exchange (Scheme 1).[4] However, it was found that direct demetallation occurred cleanly on treatment with buffered ceric ammonium nitrate in wet acetone.[5] For example, the diester 2a gave a readily separated mixture of gamma lactone 3a (29% yield), and a single hydroxy diester 4a (46% yield), both structures being assigned by IR and 200 MHz ^{1}H NMR spectroscopy.[4] The formation of 4a indicates complete stereospecificity during addition of the OH group, which we attribute to attack by water trans to the metal on an intermediate cationic dienyl-Mn(CO)$_3$ complex formed during the oxidation.[6] The structure and stereochemistry of **4a** were derived by NMR spin decoupling experiments and comparison of coupling constants with dihedral angles indicated by Dreiding models, assuming the twisted diene conformation shown.[4,7]

Similar oxidation of the methyl-substituted diester derivative **2b** again gave two products, but the gamma lactone **3b** constituted less than 5% of the mixture (from IR spectroscopy), the major product being the hydroxy diester **4b**, obtained in 70% isolated yield.[4] Similarly, the phenylsulfonyl ester gave **4c** (80% yield, 1:1 mixture of diastereomers)[4] and $\leq$5% of the corresponding gamma lactone **3c**. Thus, direct oxidative demetallation of the dienyl-Mn(CO)$_3$ system can be accomplished in good yield to give potentially useful organic products.



3 (a) R^1 = H, R^2 = CO$_2$Me

(b) R^1 = Me, R^2 = CO$_2$Me

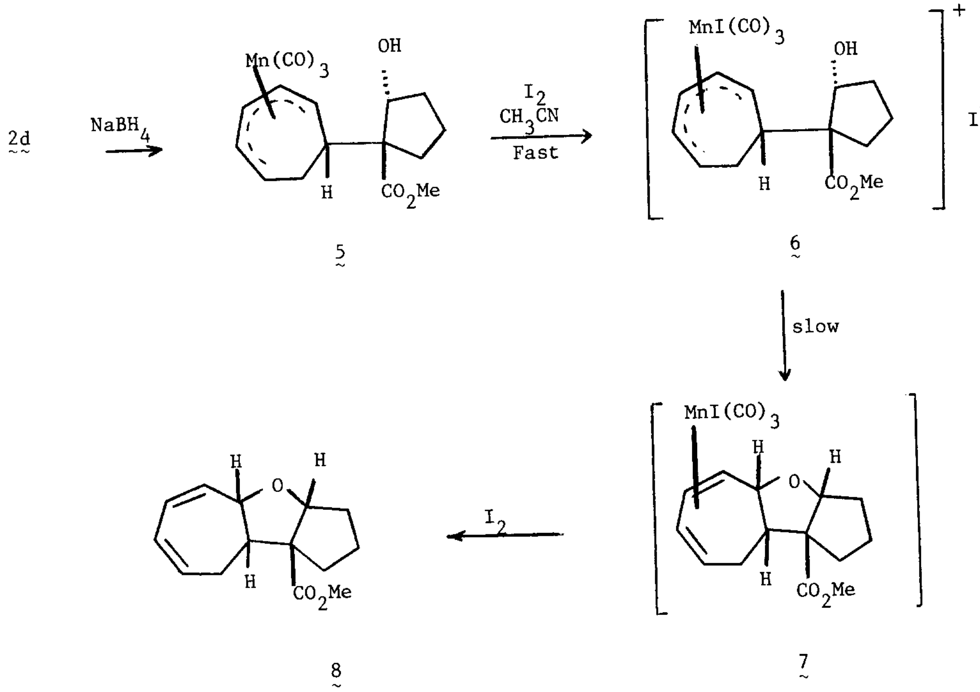
(c) R^1 = H, R^2 = SO$_2$Ph

4 (a) R = CH(CO$_2$Me)$_2$

(b) R = CMe(CO$_2$Me)$_2$

(c) R = CH(SO$_2$Ph)CO$_2$Me

Our attention was then directed at a conceptually novel approach for conversion of dienyl-Mn(CO)$_3$ complexes to organic products. We envisioned that there might be a similarity in behavior between η^3-allyl-metal complexes, η^5-dienyl complexes and uncomplexed olefins containing an attached nucleophilic group. For example, it is well-known that γ,δ-unsaturated acids undergo iodolactonization and related reactions,[8] and we were intrigued by the possibility of using the ability of the metal in these complexes to undergo addition of electrophilic species in order to promote analogous cyclofunctionalization. Conversion of ester derivatives such as **2a** to carboxylic acids proved troublesome, so we investigated cycloetherification of the hydroxy ester **5**, readily obtained by sodium borohydride reduction of keto ester **2d** (one diastereoisomer is shown for clarity). Treatment of **5** with excess of iodine in acetonitrile at 0°C resulted in an immediate change in the IR spectrum: the CO bands for **5** at 2010 and 1935 cm^{-1} were replaced by two new bands at 2075 and 1980 cm^{-1}. The higher frequency of these suggested a cationic intermediate to which we tentatively assign the structure **6** (Scheme 2). Further change in the IR spectrum was slower, gradual disappearance of the 2075, 1980 cm^{-1} absorption being accompanied by formation of low intensity bands at 2012 and 1940 cm^{-1}, which we have ascribed to a steady-state concentration of the cyclised diene complex **7**. This is readily oxidized by the iodine present to give the cycloheptadiene derivative **8**, the isolated product (75% yield, 1:1 mixture of diastereoisomers).[4] Thus, a cyclofunctionalization/demetallation procedure, which is somewhat analogous to uncomplexed alkene cyclofunctionalization, may be realised for dienylmanganese complexes, and we envisage that similar procedures will allow manipulation of other awkward organometallic systems. These aspects, together with more detailed mechanistic study, will form the basis of future investigations.



Acknowledgements

We are grateful to SERC (Great Britain) and National Institutes of Health for generous financial support of our programs and to National Science Foundation for a grant toward the purchase of the Varian XL-200 NMR spectrometer used in these studies. (CHE 80-24633).

References and Notes

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4) All new compounds were obtained as racemic mixtures and were fully characterised by IR and ^{1}H NMR spectroscopy, high resolution mass spectrometry and/or combustion analysis. Selected spectral data is as follows: **2a**: IR ($CHCl_3$) ν_{max} 2008, 1950, 1735, cm^{-1}; NMR ($CDCl_3$) δ 5.81 (1H, t, J = 6 Hz, 3-H), 5.31 (1H, dd, J = 8, 6 Hz, 2-H), 4.88 (1H, dd, J = 8, 6 Hz, 4-H), 3.74 (3H, s, CO_2Me), 3.68 (3H, s, CO_2Me), 3.55 (1H, m, obscured, 5-H) 3.48 (1H, m, 1-H), 3.01 (1H, d, J = 6 Hz, malonate CH), 2.07 (1H, m, 6-H), 1.22 (1H, m, endo-7-H), 0.91 (1H, m, exo-7-H). **3a** IR (CCl_4) ν_{max} 1780, 1730 cm^{-1}; NMR ($CDCl_3$) δ 6.05 (4H, m, olefinic), 5.16 (1H, d, $J_{3,4}$ = 7.25 Hz, 3-H), 3.79 (3H, s, CO_2Me), 3.46 (1H, d, $J_{2,3}$ = 7.0 Hz, 2-H), 3.34 (1H, complex m, $J_{3,9\alpha}$ = ca 11 Hz, $J_{2,3}$ = 7.0 Hz, $J_{3,4}$ = 7.25 Hz, $J_{3,9\beta}$ = 3 Hz, 3-H), 2.26 (2H, m, 2x9-H). **4a**: IR (CCl_4) ν_{max} 3600, 1735, 1725 cm^{-1}; NMR ($CDCl_3$), δ 5.95 (4H, m, olefinic), 4.29 (1H, m, $J_{1,7\alpha}$ = $J_{1,7\beta}$ 3 Hz, fine coupling unresolved, 1-H), 3.74 (6 H, s, $2xCO_2Me$), 3.57 (1H, d, J = 6 Hz, malonate CH), 2.94 (1H, ddm, $J_{1',6}$ = 6 Hz, $J_{6,7\alpha}$ = 10 Hz, fine coupling unresolved, 6-H), 2.25 broad (1H, s, OH), 2.07 (1H, dd, J_{gem} = 14 Hz, $J_{1,7\beta}$ = 3 Hz, 7β-H), 1.72 (1H, ddd, J_{gem} = 14 Hz, $J_{1,7\alpha}$ =3 Hz, $J_{6,7\alpha}$ = 10 Hz, 7α-H).

5) The procedure is as follows: to a stirred solution of the complex (300 mg) in reagent grade, undried acetone is added hydrated sodium acetate (900 mg) followed by portions of ceric ammonium nitrate (100 mg each) at 5 min intervals until reaction is complete, as indicated by carbon monoxide evolution at each addition. Aqueous work up and ether extraction in the usual way affords the product, purified by preparative TLC on silica gel, or HPLC.

6) A few instances of cis nucleophile addition to 18-electron transition metal complexes are known, where borohydride is the nucleophile. See ref. 1. Methoxide has been shown to undergo addition to certain dienyl complexes to give the trans adduct as the kinetic product, but the cis adduct as a thermodynamic product. See: Bryan, E. G.; Burrows, A. L.; Johnson, B. F. G.; Lewis, J.; Schiavon, G. M.; J. Organomet. Chem., 1977, 129, C18; Burrows, A. L.; Hine, K.; Johnson, B. F. G.; Lewis, J.; Parker, D. G.; Poe, A.; Vichi, E. J. S.; J. Chem. Soc. Dalton Trans., 1980, 1135. Under the conditions of our experiment, it is unlikely that similar equilibration to "thermodynamic" products is obtained.

7) The conformation of cycloheptadiene is a subject of uncertainty. A twisted diene conformation has been proposed from ^1H NMR experiments, see: Crews, P.; Chem. Comm., 1971, 583; A planar diene, experiencing severe angle strain to gain stability by conjugation, has been suggested from UV, vibrational spectroscopy and vapour phase electron diffraction methods, see: Schrader, B.; Ansmann, A.; Angew. Chem. Int. Ed. Engl., 1975, 14, 364; Chaing, J. F.; Bauer, S. H.; J. Am. Chem. Soc., 1966, 88, 420; Hagen, K.; Traetteberg, M.; Acta Chem. Scand., 1972, 26, 3643. Chemical studies in our laboratory on cycloheptadienylacetic acid derivatives are consistent with a favoured twisted diene conformation. Assuming this conformation the coupling constant data for compounds 4 are consistent only with a cis arrangement of OH and R groups, since the corresponding trans stereochemistry would give $J_{1,7\beta}$ ca 10-12 Hz (dihedral angle ca 180°).

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(Received in USA 7 November 1983)