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LETTERS

Synthesis of [2,3]-Fused Bicyclic Cyclopentadiene Derivatives by the Cycloaddition Reaction of Diyne with Methylmanganese Carbonyl Complex

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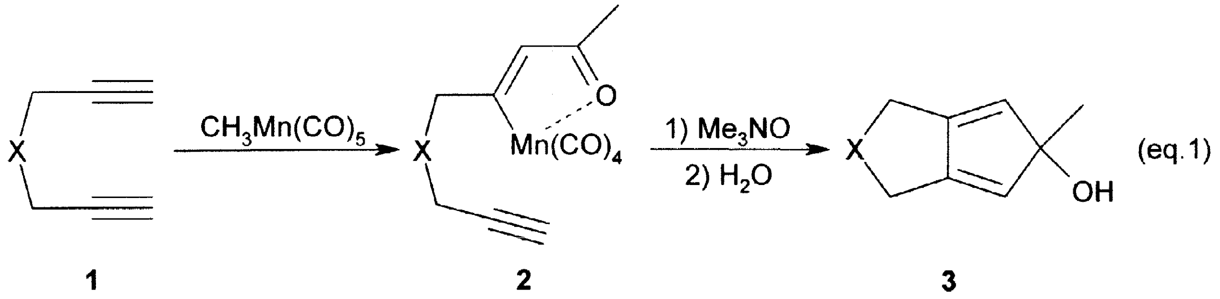
Abstract: Methylmanganese pentacarbonyl-mediated transformation of diyne to [2,3]-fused bicyclic cyclopentadienes has been carried out.

Transition metal-mediated carbocyclization of alkenes, alkynes, and enynes has been widely accepted as a synthetically useful methodology for the synthesis of cyclic and polycyclic compounds.[1] Many transition metal complexes have been used to construct ring systems from readily available substrates. However, the use of manganese complexes has been relatively rare.[2] Recently we reported the synthesis of cyclopentanoids via enyne cycloaddition using methylmanganese carbonyl complex.[3] In a continuing effort of our investigation into the manganese-mediated carbocyclization of 1,6-diyne, we discovered a novel transformation of 1,6-diynes to [2,3]-fused bicyclic cyclopentadiene derivatives, which can be served as attractive intermediates for the syntheses of a variety of polyfunctionalized cyclopentanoids. In this letter, we wish to report that a very unique carbonylative MeMn(CO)$_5$-mediated carbocyclization of 1,6-diynes gives [2,3]-fused bicyclic cyclopentadiene derivatives by incorporating carbon monoxide and a methyl group (acetyl group) as hydroxy and methyl groups (eq. 1).



A representative experimental details is as follows: A stirred solution of diyne **1b** (0.244 g, 0.82 mmol) in Et$_2$O (10 mL) was treated with a solution of MeMn(CO)$_5$[4] (0.170 g, 0.81 mmol) in Et$_2$O (5 mL) at room temperature. After the reaction mixture was stirred for 12 h, the solution was concentrated and chromatographed on a silica gel column (hexane-diethyl ether, v/v, 60:1). The yield of **2b** (entry 2 in Table 1) was 0.203 g (50 %).[5] A solution containing **2b** (70 mg, 0.138 mmol) in 10 mL of THF was treated with Me$_3$NO (26 mg, 0.346 mmol) at room temperature and the mixture was stirred for 12 h. At the end of this time, the solution was treated with 1-2 drops of H$_2$O, and the solution was stirred for 2 h. After evaporation of the solvent, the residue was chromatographed on a silica gel column (hexane-diethyl ether, v/v, 5:1). Compound **3b** (entry 2 in Table 1) was obtained in 83 % yield (39.7 mg).[6] Compounds **3** are stable in neat

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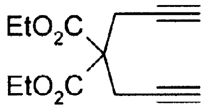
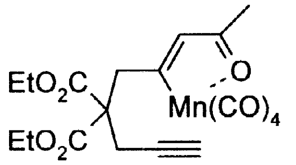
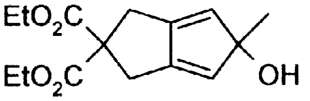
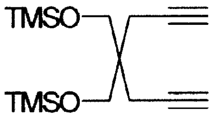
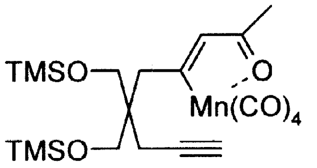
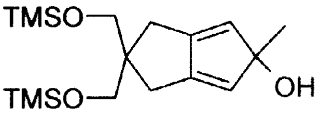
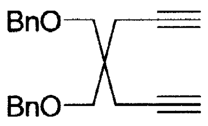
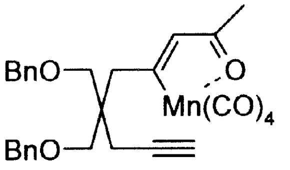
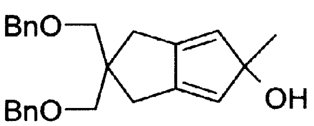
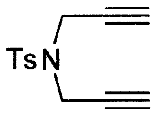
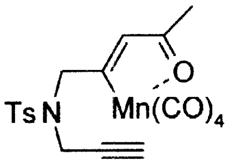
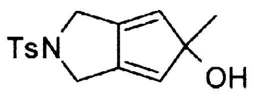
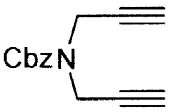
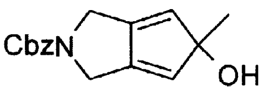
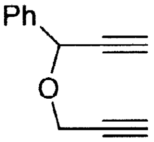
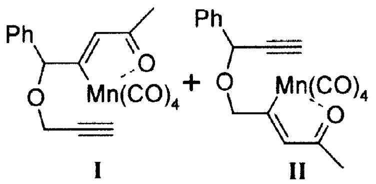
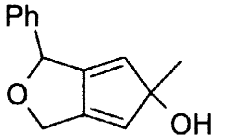
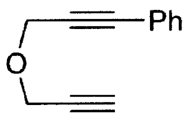
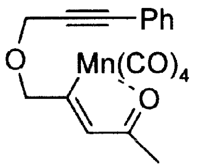
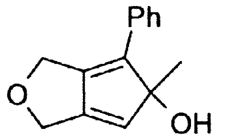
form for ca. 1 h. Compounds **3** are quite stable in a dilute acetone solution, but easily decomposed in a concentrated solution.

Table 1. Diyne cycloaddition using CH$_3$Mn(CO)$_5$ [a]

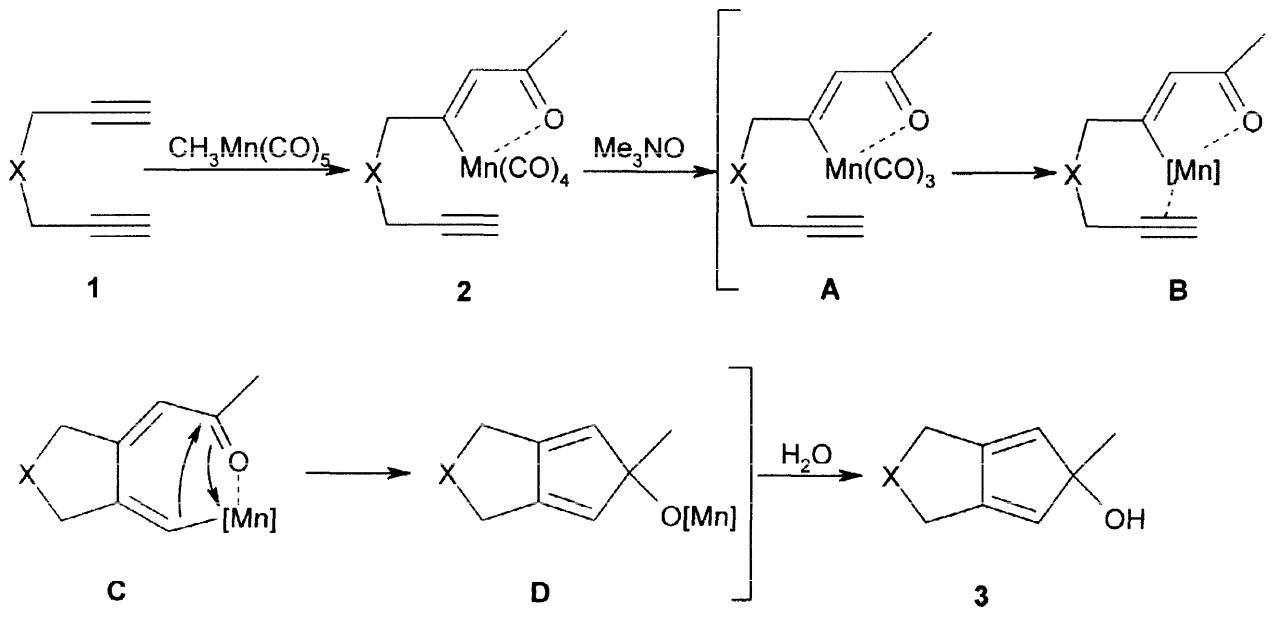
entry	**1** (diyne)		Yield(%) of **2**		Yield(%) of **3**	
1		**a**		55		90
2		**b**[b]		50		83
3		**c**		41		71
4		**d**		72		52
5		**e**	[c]			20[d]
6		**f**	 I II	92		56
7		**g**		88		64

[a]Isolated yield. [b]TMS = SiMe$_3$ [c]Compound **2** was not isolated. [d]Overall yield from **1**

A series of diynes **1a-g** were subjected to react with MeMn(CO)$_5$ to produce manganacycles **2**.[7] Formation of **2** involved a migratory insertion of a methyl group and a subsequent insertion of alkyne between manganese and acetyl group. The reaction is quite straightforward and compounds **2** are easily obtained in reasonable to high yields. However, when the diyne substrate was **1e**, the corresponding manganese complex **2e** was not easily separated from the reaction mixture. Thus, for **1e**, the corresponding manganacycle **2** was not isolated and the reaction mixture was used to a further reaction. For the substrate **1f**, **2f-I** and **-II** were obtained in the ratio of 1:0.9. Compounds **2** are stable to handle in air.

Compounds **2a-g** were subjected to bicyclization in the presence of Me_3NO to afford the corresponding [2,3]-fused bicyclic cyclopentadienes (Table 1). Me_3NO was used to generate a reactive 16-electron species.[8] Formation of **3** from **2** is quite similar to the reaction of orthomanganated acetophenone with alkynes to yield inden-1-ols.[2e-j] This manganese-mediated cyclization is applicable to a range of substrate types including those containing protected ketones (entries 2 and 3) and those with a heteroatom in the propargylic position (entries 4-7) giving in each case good yields. Mono-substituted internal alkyne (entry 7) was also shown to undergo facile cyclization.

A possible reaction pathway for the cyclization of 1,6-diynes is illustrated in Scheme 1. A coordinatively unsaturated manganese complex **2A** generated by treatment of **2** with Me_3NO would coordinate to free triple bond to form **B**. Intermediate **B** could undergo an intramolecular cyclization to form **C**, and a subsequent migration of manganese carbonyls and a cyclization to afford **D**. Demetallation by hydrolysis would give **3**. Although we believe that this reasonable reaction sequence is likely,[2d-i] none of the suggested intermediates has been detected so far.



Scheme 1

In summary, we have found a novel transformation of diynes to [2,3]-fused bicyclic cyclopentadiene derivatives using $MeMn(CO)_5$. Further studies of this reaction and its application to organic synthesis are currently in progress.

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5. IR: ν(CO) 2066, 1978, 1932 cm^{-1}, ν(C=O) 1568 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.15 (s, 1 H), 3.54 (s, 4 H), 3.31 (s, 2 H), 2.31 (d, 2.5 Hz, 2 H), 2.29 (s, 3 H), 2.03 (t, 2.5 Hz, 1 H), 0.11 (s, 18 H) ppm; HRMS (M^+) calcd. 506.0989, obsd. 506.0994.
6. IR: ν(OH) 3408 cm^{-1}; ^{1}H NMR (300 MHz, aetone-d_6): δ 5.56 (dd, 1.4, 1.6 Hz, 2 H), 3.73 (s, 1 H), 3.46 (s, 2 H), 3.45 (s, 2 H), 2.20 (dd, 1.4, 17.0 Hz, 2 H), 2.09 (dd, 1.6, 17.0 Hz, 2 H), 1.37 (s, 3 H), 0.09 (s, 9 H), 0.08 (s, 9 H) ppm; ^{13}C NMR (75.5 MHz, aetone-d_6): δ 149.33, 132.81, 92.61, 66.45, 66.11, 56.23, 31.89, 25.11, 0.62, 0.56 ppm; HRMS (M^+) calcd. 340.1890, obsd. 340.1899.
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