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Synthesis of Cyclopentanoids via Enyne Cycloaddition Reaction Using Methylmanganese Carbonyl Complex

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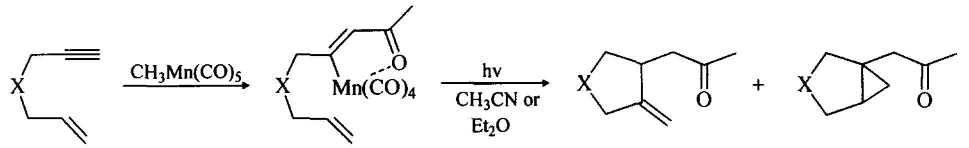
Abstract: Methylmanganese pentacarbonyl-mediated transformation of enynes to cyclopropanated bicyclic compounds and cyclopentanes bearing an exocyclic double bond has been carried out. Control of the product distribution can be achieved by changing reaction conditions.

The development of new metal-promoted methods for the construction of ring systems has been an important ongoing challenge for synthetic chemists.[1] Many transition metal complexes have been used to construct ring systems from readily available substrates.[2] However, the use of manganese complexes to build ring carbon skeletons has relatively been rare: treatment of alkyl- and aryl-manganese pentacarbonyl complexes with alkenes was reported to yield butenolides or cyclized compounds.[3] The rarity of the use of manganese compounds prompted us to search for a manganese mediated cyclization reaction of enyne. In this letter, we wish to report the transformation of enynes to cyclopropanated bicyclic compounds and cyclopentanes bearing an exocyclic double bond (eq. 1). It is of a particular note that the product distribution can be easily controlled by changing the reaction medium.

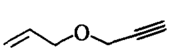
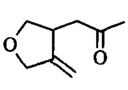
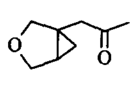
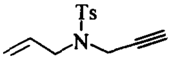
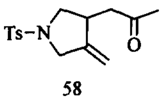
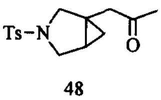
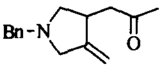
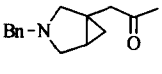
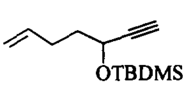
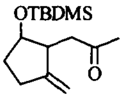
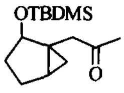
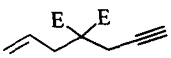
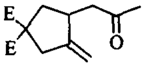
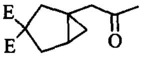
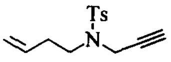
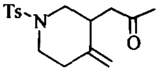
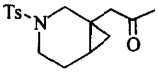
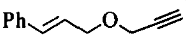
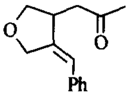
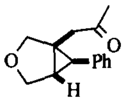
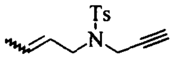
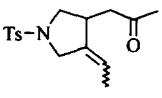
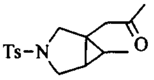
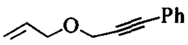


(eq.1)

2 3A 3B

Compounds, $CH_3Mn(CO)_5$[4] (**1**) (0.406 g, 1.94 mmol) and enynes (0.452 g, 1.90 mmol) (entry 5 in Table 1), were dissolved in 30 mL of diethyl ether at room temperature. The solution was stirred for 3 days. The colorless solution turned into a clear yellow. After evaporation of the solvent, the residue was column chromatographed on silica gel by eluting hexane/diethyl ether (v/v, 10:1). The yield of **2** (entry 5 in Table 1) was 0.38 g (45%). Compound **2** (0.133 g, 0.30 mmol) was dissolved in 30 mL of diethyl ether. The solution was irradiated with medium pressure mercury lamp for 1.5 h. The solution was then exposed to air. The solution turned brown. After filtration of the brown precipitates, the filtrate was concentrated and column chromatographed on silica gel by eluting with hexane/diethyl ether (v/v, 2:1 - 1:1). Compound **3A** (entry 5 in Table 1) was obtained in 54% yield.[4a] In the same way as above, **2** was dissolved in acetonitrile and irradiated. After purification, **3B** (entry 5 in Table 1) was obtained in 51% yield.[4b] For the reaction of trapping with D_2O (0.10 - 0.13 g of **2** was used, entry 5 in Table 1), the same experimental procedure as above was applied except addition of 2 drops of D_2O instead of exposure to air. In diethyl ether **3A** was obtained in 49% yield and in acetonitrile **3B** was obtained in 47% yield. The degrees of deuterium incorporation in **3A** and **3B** were 100%.

Table 1. Enyne cycloaddition reaction using $CH_3Mn(CO)_5$[a]

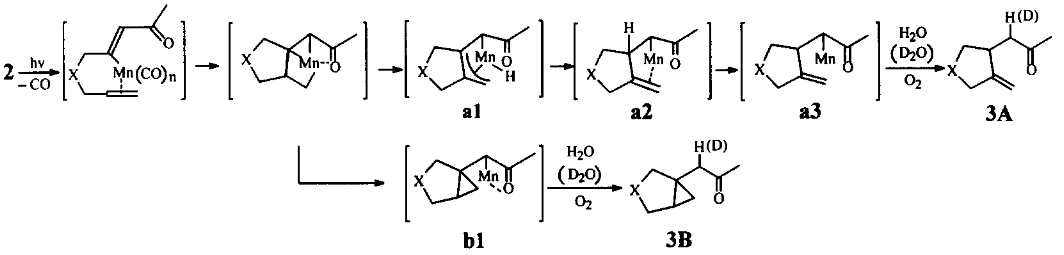
Entry	Enyne	Yield (%) of 2	Yield (%) of 3			
			Et_2O		CH_3CN	
			A	B	A	B
1		78	 58	0	0	 66
2		87	 58	0	8	 48
3		52	 38	11	0	 52
4		74	 60	5	9	 71
5		45	 54	0	0	 51
6		74	 30	 12	0	[b]
7	[c]	92	 38[d]	 28[e]	0	[b]
8	[f]	75[g]	 16[h]	 52[i]	0	17[b,j]
9		45	0	0	0	0

[a] Isolated yield. [b] In runs 6, 7, and 8, propargyl-N, propargyl-O, propargyl-N bond-cleaved compounds were isolated as major products (89%, 68%, 58%, respectively). [c] Trans isomer. [d] *(Z)* isomer. [e] *(rel-1R,5S,6S)* isomer. [f] An isomeric mixture (trans/cis = 3:1). [g] Trans/cis = 3:1 [h] Isomeric ratio = 1.2:1 [i] Isomeric ratio = 3:1 [j] Isomeric ratio = 1.6:1

The reaction involved a migratory insertion of a methyl group and a subsequent insertion of alkyne between manganese and acetyl group.[5] Compounds **2** were quite stable. The reactions proceeded at atmospheric pressure.

Photolysis can be carried out in any hydrocarbon solvent provided that **2** is soluble and stable in those solvents. However, the best results were obtained in CH_3CN and Et_2O. Unfortunately, some **2** (entries 6 and 7 in Table 1) did not produce the expected products in CH_3CN. Instead, heteroatom-carbon bond-cleaved compounds were isolated as major products. Oxygen was required to liberate the organic ligand from the metal. Thus, the reaction mixture must be exposed to air for the product formation. Assignment of structures **3A** and **3B** (Table 1) was derived from their spectral data and comparison to the known compounds.[6-8] New compounds were characterized by IR, ^1H NMR, ^{13}C NMR, and high resolution mass. Reasonable yields were obtained using substrates in which alkene and alkyne were connected with a three- or four-atom chain. However, an internal alkyne is not a suitable substrate (entry 9 in Table 1). For an internal alkyne, no major products were isolated after workup. The effect of alkene substitution on this transformation was studied (entries 7 and 8). The combined yields for **A** and **B** in diethyl ether were *ca* 66 - 68%. For entry 7, a *trans*-enyne was employed and the final product **A** was a *Z* isomer and **B** was a *rel-1R,5S,6S* isomer. The geometric integrity was retained in **B**, but not in **A**. For entry 8 in Table 1, an isomeric mixture (*trans* : *cis* = 3:1, determined by ^1H NMR (500 MHz)) was used as an enyne substrate. Surprisingly, in diethyl ether, **B** was obtained as a major product and the isomeric ratio was retained. For **A**, the isomer ratio was reversed to 1: 1.2. The steric effect of the substituent on the alkene may be responsible for the product distribution.

The most probable sequence of the present process is CO loss to give a 16-electron species, followed by coordination of the double bond as an η^2 ligand, subsequent intramolecular cyclization, and metal elimination to give **A** or **B** depending on the reaction routes (Scheme 1). Although a reasonable reaction sequence can be proposed, none of the suggested intermediates has been detected so far.



Scheme 1

The pathway to **A** may involve an intramolecular cyclization, the intermediary of η^3-allylmanganese hydride **a1**, subsequent migration of hydride to generate intermediate **a2**, liberation of alkene (**a3**), and finally demetalation to **A**. The pathway to **B** may involve an intramolecular cyclization, cyclopropanation to **b1**, and demetalation to **B**.[9] When the demetalation was done in the presence of D_2O, deuterium was found at the α-methylene position to the ketone. Thus the demetalation generated the anionic carbon that underwent protonation by water during workup.

The advantages of the reaction described in this letter are 1) efficient formation of five and six membered rings, 2) mild reaction conditions, and 3) easy control of the distribution of reaction products.

In conclusion, we have demonstrated the easy transformation of enynes to cyclopropanated bicyclic compounds and cyclopentanes bearing an exocyclic double bond using $MeMn(CO)_5$. Recently Jennings *et al.*[10] reported the platinum(II)-catalyzed isomerization of bicyclic alkoxycyclopropanes to 2-methyl ketones. Further studies of this reaction and its application to organic synthesis are currently in progress.

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References and Notes

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9. One of the reviewer suggested an alternative pathway to **b2** in the reaction mechanism: insertion of double bond into carbon-Mn bond to produce alkyl-Mn complex, and then -unsaturated olefin insets into alkyl-Mn complex to give **b2**.
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