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SYNTHESIS OF ENONES AND BUTENOLIDES USING ORGANOMANGANESE PENTACARBONYL COMPLEXES.[1]

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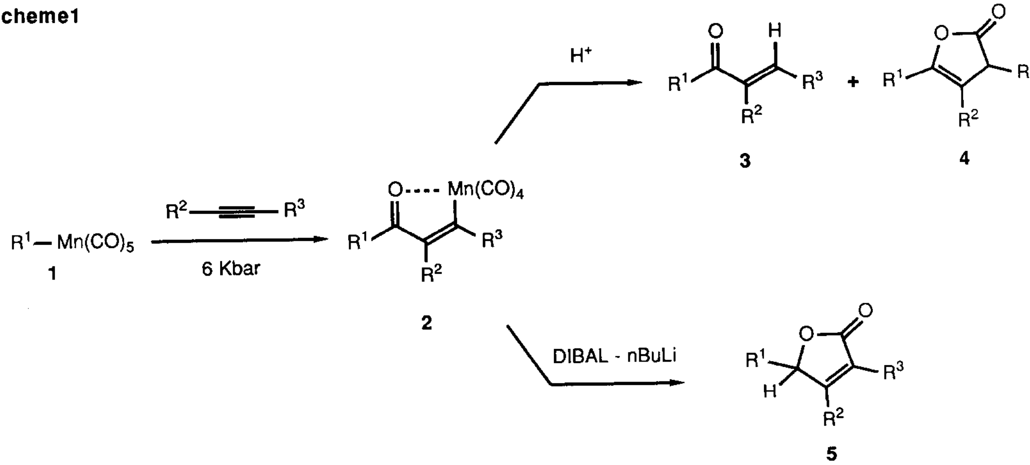
This manuscript is dedicated to George H. Büchi on the occasion of his 65th birthday.

Abstract Sequential insertion of carbon monoxide and alkynes into alkylmanganese pentacarbonyl complexes at pressures of 6 kbar provides unsaturated manganacycles in a regioselective manner. The manganacycles can be transformed under acidic conditions into a mixture of enone and furanone. Alternatively, themanganacycle can be reduced with DIBAL-ate complex to furnish the butenolide.

In the preceding Communication, we demonstrated that alkylmanganese pentacarbonyl complexes (**1**) reacted with selected alkenes at pressures of 6 kbar to produce manganacycles arising from the sequential insertion of carbon monoxide and the alkene into the carbon-manganese bond. These manganacycles were demetalated by photolysis in the presence of molecular oxygen to produce highly functionalized carbonyl compounds.[2] The overall transformation resulted in the formation of two carbon-carbon bonds, incorporation of one molecule of carbon monoxide, and the regio- and stereoselective attachment of an acyl residue to the alkene. In this Communication, we report that alkynes also participate in the sequential insertion process with alkylmanganese pentacarbonyl complexes (**1**) to yield manganacycle **2**. Subsequent treatment of **2** with acid yields a mixture of enone **3** and furanone **4**; whereas, reduction of the manganacycle with DIBAL-ate complex gives the corresponding butenolide **5** (Scheme 1).

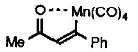
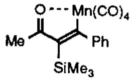
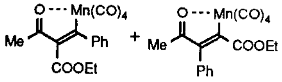
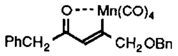
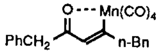
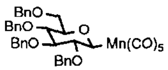
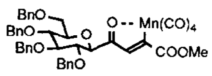
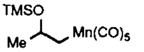
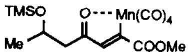
Scheme1



As indicated in Table 1, terminal alkynes react with structurally diverse alkylmanganese pentacarbonyl complexes (1) at pressures of 6 kbar [4] to produce manganacycle **2** in moderate to good yields. For instance, methylmanganese pentacarbonyl (**1**, R^1 = Me) furnished the respective adduct with phenylacetylene in a regiospecific manner in 65% yield under high pressure conditions (Table 1, entry 1). Likewise, benzylmanganese pentacarbonyl and 1-hexyne reacted to produce the corresponding manganacycle in a completely regioselective manner (entry 5).

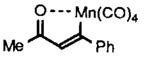
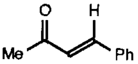
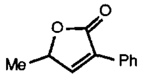
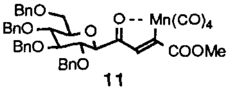
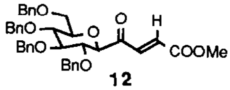
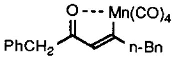
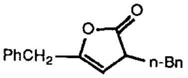
Disubstituted alkynes also underwent the sequential insertion process with manganese complexes; however, in some instances regioisomeric products were obtained. Trimethylsilyl phenylacetylene, for instance, reacted with the methylmanganese complex to furnish a single regioisomer (entry 2). On the other hand, ethyl phenylpropiolate and the methyl complex furnished a mixture of manganacycles **6** and **7** in a ratio of 1.5:1. This result suggests that high regioselectivity will be observed with disubstituted alkynes only in those instances in which the substituents on the alkyne differ in electronic properties.

Table 1. Formation of Manganacycle **2** at 6 kbar.

Entry	Manganese Complex (1)	Alkyne	Manganacycle 2	Yield (%)
1	Me - $Mn(CO)_5$	$H-\!\!\equiv\!\!-Ph$		67
2	"	$Me_3Si-\!\!\equiv\!\!-Ph$		55
3	"	$Ph-\!\!\equiv\!\!-COOEt$	 **6** **7** **6** : **7** = 1.5 : 1	85
4	$PhCH_2$ - $Mn(CO)_5$	$H-\!\!\equiv\!\!-CH_2OBn$		50
5	"	$H-\!\!\equiv\!\!-n\text{-}Bn$		65
6		$H-\!\!\equiv\!\!-COOMe$		80
7		$H-\!\!\equiv\!\!-COOMe$		65

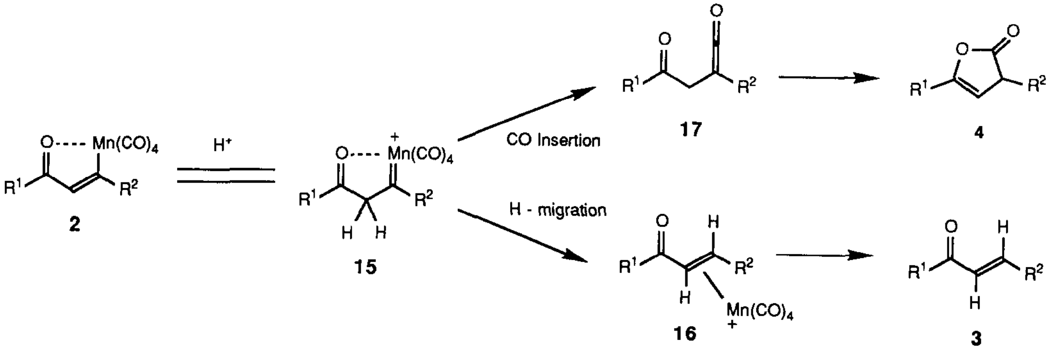
Unlike manganacycles resulting from sequential insertion of alkylmanganese pentacarbonyl complexes with alkenes[2], unsaturated manganacycle **2** failed to demetalate upon photolysis. Removal of the metal was accomplished, however, under two sets of reaction conditions and the results are summarized in Tables 2 and 3. Treatment of manganacycle **2** with HCl in acetonitrile resulted in formation of a mixture of enone **3** and furanone **4**. The ratio of enone to furanone produced in the reaction depended upon the electronic characteristics of the substitutents attached to C-2 of the manganacycle. For instance, acid treatment of complex **8** gave an 80% yield of a mixture of enone **9** and butenolide **10** in which enone predominated (Table 2, entry 1). Acidolysis of glucosyl complex **11**[1] yielded exclusively enone **12**

Table 2. Acidolysis of Manganacycle **2**.

Entry	**Manganacycle 2**	**Products**	**Yield (%)**
1	 **8**	 **9** +  **10** **9** : **10** = 3.2 : 1	80
2	 **11**	 **12**	65
3	 **13**	 **14**	65

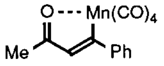
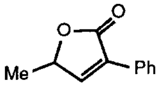
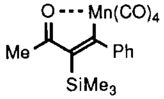
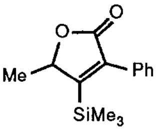
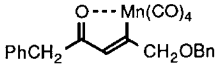
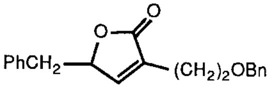
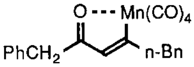
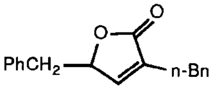
(entry 2). In stark contrast, manganacycle **13** underwent demetalation to produce furanone **14** as the sole product. We propose that these products arise according to the mechanism shown in Scheme 2. Reversible protonation of manganacycle **2** generated cationic complex **15** which had two manifolds for further reaction. Hydrogen migration in **15** produced alkene complex **16** and ultimately enone **3** following demetalation.[5] Alternatively, **13** suffered CO insertion into the metal carbene bond yielding ketene **17**[6] which underwent ring closure following enolization to produce furanone **4**. The butenolide arose from acid-catalyzed alkene isomerization of the furanone.

Scheme 2



Butenolide **5** is available, alternatively, by reduction of manganacycle **2** with DIBAL-ate complex[7] as indicated in Table 3. In these instances, hydride was delivered to the acyl function to generate the corresponding alkoxide. Migratory insertion of the organic ligand to a metal-bound CO and subsequent intramolecular Reppe reaction[8] of the resulting acylmanganese derivative led to the butenolide.

Table 3. Formation of Butenolide **5** from Manganacycle **2**.

Entry	**Manganacycle 2**	**Butenolide 5**	**Yield (%)**
1			40
2			60
3			60
4			55

Application of the sequential insertion sequence to the total synthesis of natural products will be reported in due course.

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References and Notes

1. For earlier papers in this series see (a) DeShong, P.; Slough, G. A. *Organometallics* **1984**, *4*, 636. (b) DeShong, P.; Slough, G. A.; Elango, V. *J. Am. Chem. Soc.* **1985**, *107*, 7788.
2. See preceding communication in this issue.
3. Booth and Hargreaves have demonstrated that methyl and phenylmanganese pentacarbonyl undergo sequential insertion of carbon monoxide and alkynes to produce manganacycles: Booth, B. L.; Hargreaves, R. G. *J. Chem. Soc. (A)* **1970**, 308. See also Booth, B. L.; Gardner, M.; Haszeldine, R. N. *J. Chem. Soc., Dalton Trans.* **1975**, 1856, and references cited therein. See also Booth, B. L.; Lewis, E. J. R. *J. Chem. Soc., Dalton Trans.* **1982**, 417, and references cited therein.
4. For a detailed description of the high pressure apparatus used in this study, see: DeShong, P.; Dicken, C. M.; Perez, J. J.; Shoff, R. M. *Org. Prep. Proc. Int.* **1982**, *14*, 369.
5. For examples of similar reactions in iron and rhenium complexes see Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 3761 and Halton, W. G.; Gladysz, J. A.*ibid*, **1983**, *105*, 6157.
6. Insertion of carbon monoxide into chromium carbene complexes has been observed: Yamashita, A.; Scahill, T. A. *Tetrahedron Lett.* **1982**, *23*, 3765.
7. Kims, S.; Anh, K. H. *J. Org. Chem.* **1984**, *49*, 1717. $LiBEt_3H$ and DIBAL could also be utilized in this reaction; however, a significant quantity of lactol from overreduction of the butenolide was obtained with these reagents.
8. For leading references see Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA; 1980.

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