from the C_2–C_3 σ-bond. Further experiments are planned to adduce support for this unusual observation.

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Regioselective Opening of Epoxides and Ethers by (Trialkylsilyl)manganese Pentacarbonyl Complexes. A General Strategy for the Synthesis of Spiroketal Lactone and Cyclopentenone Derivatives

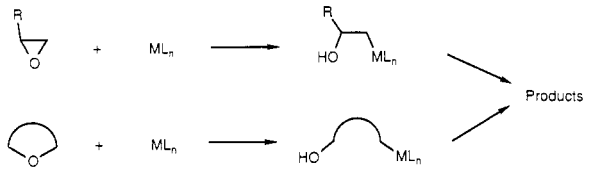
Summary: (Trialkylsilyl)manganese pentacarbonyl reagents react with epoxides and cyclic ethers in a regioselective manner to furnish functionalized alkylmanganese pentacarbonyl complexes. These complexes undergo subsequent sequential insertion with either alkenes or alkynes to afford manganacycles. Photodemetalation of the alkene-derived manganacycles give either aldol-like products or spiroketal lactone derivatives. Acid-catalyzed demetalation of alkyne adducts affords cyclopentenone derivatives by a Nazarov cyclization sequence.

Sir: Preparation of functionalized organotransition metal complexes remains as one of the major hurdles to the application of transition metal based reagents for organic synthesis.[1] On the other hand, a myriad of methods are available in the organic arsenal for the stereoselective synthesis of epoxides,[2] and epoxides should be ideal substrates for the synthesis of transition metal reagents if effective ring cleavage strategies could be effected. As outlined in Scheme I, the nucleophilic opening of an epoxide by a nucleophilic metal complex to afford a β-alkoxy complex should be a viable method of producing functionalized organotransition metal complexes for further elaboration in organic synthesis. In addition, this strategy could be extended to cyclic ethers with the expectation that regioselective ring scission would yield novel complexes poised to serve as intermediates in a wide variety of subsequent transformations (see Scheme I).

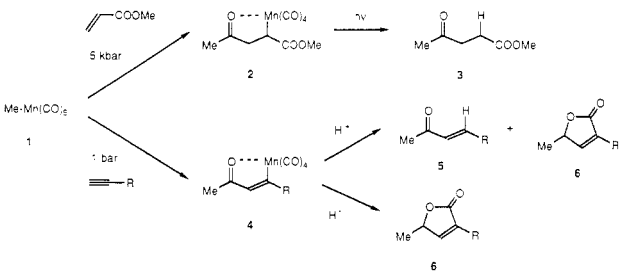
Our laboratory has recently demonstrated that alkylmanganese pentacarbonyl complexes (1) undergo sequential insertion reactions with either alkenes or alkynes to furnish unique manganese complexes (manganacycles) **2** and **4**, respectively (Scheme II). Photoinitiated demetalation of manganacycle **2** gave the 1,4-dicarbonyl derivative **3**, whereas manganacycle **4** underwent demetalation to afford either enone **5** or butenolide **6**, depending upon the specific demetalation conditions employed.[3]

A previous investigation by Gladysz had shown that TMS complex **7** reacted with epoxides and ethers to yield the corresponding (silyloxy)manganese derivatives; however, subsequent reactions of these complexes were not reported.[4,5] In this paper we report that epoxides and cyclic ethers react with (trimethylsilyl)manganese pentacarbonyl (**7**) or (*tert*-butyldimethylsilyl)manganese pentacarbonyl (**8**) to afford [(silyloxy)alkyl]manganese complexes, which are competent in the sequential insertion reactions indicated in Scheme II and furnish functionalized manganacycle derivatives. Subsequent transformations of these manganacycles lead to the production of β-hydroxycarbonyl, spiroketal lactone, and cyclopentenone derivatives.

Scheme I



Scheme II



Scheme III

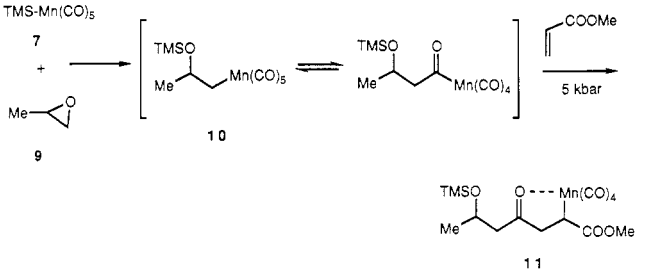


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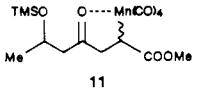
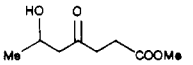
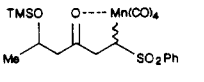
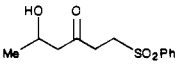
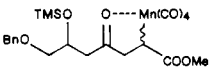
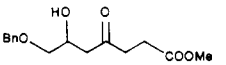
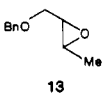
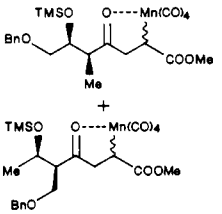
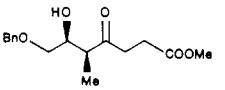
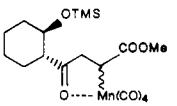
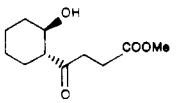
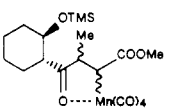
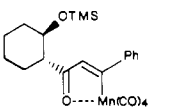
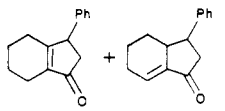
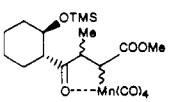
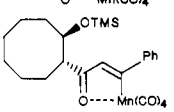
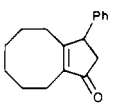
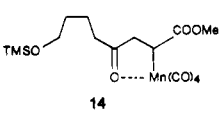
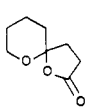
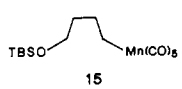
Table I

entry	epoxide	manganese reagent	alkene	sequential insertion adduct	yield,[a] %	demetalation conditions	product	yield,[a] %
1	 9	TMS-Mn(CO)$_5$		 11	82[b]	A		53
2	 9	TMS-Mn(CO)$_5$			56[b]	A		45
3	 12	TMS-Mn(CO)$_5$			48[b]	A		32
4	 13	TMS-Mn(CO)$_5$			40 (2.6:1)[b]	A		60
5		TMS-Mn(CO)$_5$			82[b]	A		60
6		TMS-Mn(CO)$_5$			40[b]			
7		TMS-Mn(CO)$_5$		 18	59	B	 19 20	35 (1:2.6)
8		TMS-Mn(CO)$_5$			65			
9		TMS-Mn(CO)$_5$		 21	99	B	 22	36
10		TMS-Mn(CO)$_5$		 14	39	A	 17	77
11	 15	TMS-Mn(CO)$_5$		16	77	A	17	77

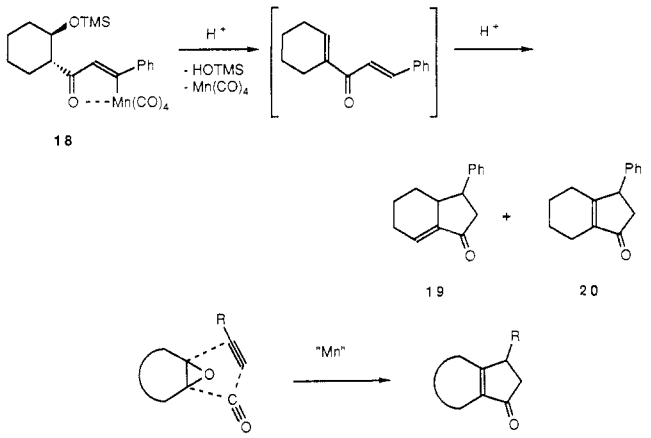
[a] Unoptimized yield of isolated product. Characterized by IR, ^{1}H and ^{13}C NMR, and MS. [b] Product obtained as a mixture of diastereomers. The diastereomer ratio was not determined. Demetalation conditions. A: (1) *hν*, 350 nm; MeCN, room temperature; 1–12 h. (2) H_2O, O_2; room temperature. B: HCOOH; H_3PO_4, 90 °C, 2 h.

(Trimethylsilyl)manganese pentacarbonyl (**7**) and (*tert*-butyldimethylsilyl)manganese pentacarbonyl (**8**) were prepared by reaction of the respective silyl triflate with sodium manganate(I) pentacarbonyl in pentane at −50 °C. This procedure afforded the silyl complexes in 60%–70% yield, which was a significant improvement over existing methods.[4]

Table I summarizes the results obtained from sequential insertion reactions of epoxides and cyclic ethers with (trimethylsilyl)manganese pentacarbonyl (**7**). In each instance, a solution of the epoxide, manganese complex **7**, and either the alkene or the alkyne was allowed to react, furnishing the sequential insertion adduct by the sequence indicated in Scheme III.[6] In this instance, [(silyloxy)alkyl]manganese reagent was generated in situ by cleavage of the epoxide moiety and subsequently underwent sequential insertion of the alkene to afford the manganacycle. For example, regiospecific opening of propylene oxide by **7** gave (β-silyloxy)manganese complex **10**, which underwent in situ migratory insertion of carbon monoxide and in-

(6) **General Procedure for the High-Pressure Preparation of Saturated Epoxide Adducts.** A polypropylene syringe was charged with an Et_2O solution of (trimethylsilyl)manganese pentacarbonyl (**7**, 0.3–0.8 mmol), epoxide (1.1–6.0 equiv), and alkene (1.1–2.0 equiv). The reaction mixture was pressurized at 5 kbar[9] for 24–96 h. The reaction mixture was depressurized, the reaction vessel was rinsed with EtOAc, and the combined organics were concentrated in vacuo. Adducts were purified by flash chromatography.

Scheme IV



sertion of methyl acrylate at 5 kbar to yield manganacycle **11**.

Alternatively, it was possible to preform the [(silyloxy)alkyl]manganese complex by reacting the epoxide with silylmanganese reagent **7** and then utilize the functionalized alkylmanganese complex for sequential insertion in a separate reaction. For instance, complex **10** was generated and characterized by the treatment of **7** with propylene oxide according to the established protocol.[4] (Silyloxy)manganese complex **10** produced in this manner also underwent sequential insertion to afford manganese complex **11** upon exposure to methyl acrylate at a pressure of 5 kbar. In practice, the simplicity of reagent manipulation and improved yields associated with the in situ procedure made it the method of choice for manganacycle formation.

Epoxide opening by **7** was completely regioselective with monosubstituted epoxides **9** and **12** and afforded adducts arising from attachment of manganese at the less hindered center. Disubstituted epoxide **13**, on the other hand, displayed modest regioselectivity in the reaction with **7**. The major adduct in this case resulted from attack of the metal at the epoxide carbon bearing the methyl group in analogy with the results of Behrens and Sharpless in this system.[7]

Silylmanganese complex **7** is sufficiently oxophilic that it will also cleave less strained ring systems than epoxides. Tetrahydrofuran (Table I, entry 11) and oxetane[4] underwent ring cleavage with **7** to afford the corresponding (silyloxy)manganese pentacarbonyl complexes.

(Silyloxy)manganese complexes resulting from opening of epoxides and tetrahydrofuran by silyl complex **7** were competent to participate in the sequential insertion reaction with either alkenes or alkynes as indicated by the results in the table. They display comparable regioselectivity and stereoselectivity with regard to alkene/alkyne insertion as was observed for simple alkylmanganese pentacarbonyl complexes (see **1**, Scheme I).[3] For example, the in situ opening of tetrahydrofuran by the (trimethylsilyl)manganese complex **7** followed by sequential insertion of methyl acrylate gave unstable manganacycle **14**. An analogous cleavage of tetrahydrofuran by (*tert*-butyldimethylsilyl)manganese pentacarbonyl (**8**)[8] yielded the isolable manganese complex **15** in 55% yield. Manganacycle **16**, the TBS analogue of **14**, was prepared by sequential insertion into **15**.

Manganacycles resulting from sequential insertion of alkenes (entries 1–7, 11, 12; Table I) underwent photoinitiated demetalation by using the established protocol to afford β-hydroxycarbonyl derivatives in moderate yields.[3] The hydroxycarbonyl derivatives arising from demetalation/desilylation of manganacycles **14** and **16**, respectively, cyclized upon exposure to acidic media to give spiroketal lactone **17**.

Acid-catalyzed demetalation of alkyne-derived manganacycles failed to yield the anticipated enone or butenolide derivative; instead, cyclopentenone derivatives were isolated. For example, when manganacycle **18** was subjected to acidic conditions, a mixture of cyclopentenones **19** and **20** (**19**:**20** = 1:2.6) was obtained in 35% yield. Similarly, treatment of manganacycle **21** with acid furnished bicyclic enone **22**. Presumably, the cyclopentenones result from Nazarov cyclization[9] as depicted in Scheme IV involving initial loss of the elements of trialkylsilanol to give a cross-conjugated dienone required for the electrocyclic ring closure. The two-step process of sequential insertion and Nazarov cyclization constitutes a formal cyclopentenone annulation process in which manganese mediates the condensation between an epoxide, carbon monoxide, and an alkyne.

In conclusion, we have demonstrated that the adducts resulting from reaction of (trialkylsilyl)manganese pentacarbonyl complexes with epoxides/cyclic ethers can be utilized for the stereo- and regioselective synthesis of β-hydroxycarbonyl, spiroketal lactone, and cyclopentenone derivatives. The application of this methodology to the total synthesis of natural products will be reported in due course.

Acknowledgment. We thank the National Institutes of Health (Grant GM 37014 and AI 23688) for generous financial support. We also thank Dr. Jim Rice for help in obtaining mass spectral data.

(7) Behrens, C. H.; Sharpless, K. B. *J. Org. Chem.* **1985**, *50*, 5696.
(8) Prepared in situ by the reaction of *tert*-butyldimethylsilyl triflate and sodium manganate in pentane at −20 °C.
(9) For a review of the Nazarov cyclization reaction, see: Santelli-Rouvier, C.; Santelli, M. *Synthesis* **1983**, 429. For additional examples of Nazarov cyclization see: (a) Brande, E. A.; Coles, J. A. *J. Chem. Soc.* **1952**, 1430. (b) Hirano, S.; Takagi, S.; Hiyama, T.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 169. (c) Jones, T. K.; Denmark, S. E. *Helv. Chim. Acta* **1983**, *66*, 2377. (d) Jones, T. K.; Denmark, S. E. *Helv. Chim. Acta* **1983**, *66*, 2397.
(10) A description of the high-pressure apparatus can be found in DeShong, P.; Dicken, C. M.; Perez, J. J.; Shoff, R. M. *Org. Prep. Proced. Int.* **1982**, *14*, 369.

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Cyclopentanoid Synthesis via Directed Cationic Cyclizations. Efficient Generation and Rearrangement of the Intermediate Cyclohexyl Cation

Summary: Acyclic acetals in the presence of $SnCl_4$ initiate a cationic cyclization pathway, which is directed to cyclopentanoid ring formation via a pinacol rearrangement step.

Sir: Carbocation–olefin cyclizations represent a powerful method to construct 6-membered carbocyclic[1] and 5- to

(1) For a recent review, see: Bartlett, P. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: Orlando, 1984; Vol. 3, Chapter 5.

0022-3263/88/1953-4894$01.50/0