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Triallylmanganate-Mediated Cyclization of Diyne, Enyne, and Diene. An Unprecedented Bicyclization Reaction into Bicyclo[5.3.0]decane and Bicyclo[4.3.0]-nonane Skeletons

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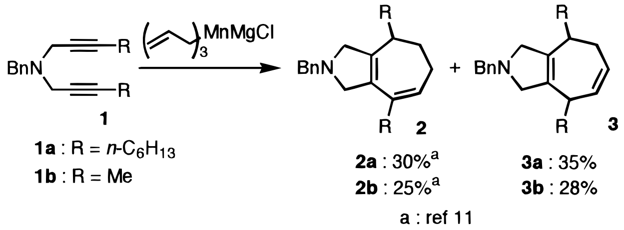
Summary: Treatment of diynes with triallylmanganate provided bicyclized products containing a seven-membered ring. N,N-Bis(2-nonynyl)benzylamine gave a mixture of 9-benzyl-2,6-dihexyl-9-azabicyclo[5.3.0]deca-1(7),2-diene, and 9-benzyl-2,6-dihexyl-9-azabicyclo[5.3.0]deca-1(7),3-diene, upon treatment with triallylmanganate.

Transition metals have become indispensable tools in organic synthesis. Nowadays, methodological progress and new reactions are mostly based on the use of transition metals or organometallic materials. Transition metals or metal−ligand complexes ML_n are able to make molecules in their coordination sphere react intramolecularly or intermolecularly in high order which would normally not be realized.[1] Among these organometallic reactions, group IV metallocene-mediated cycloaddition reactions[2,3] of diynes, enynes, and dienes have been widely and intensively researched and become powerful methods for the construction of cyclic-compounds. Other transition-metal-assisted cycloaddition reactions, such as with use of Ni,[4] Pd,[5] Co,[6] and Ru,[7] have also been extensively studied. In contrast, manganese-assisted intramolecular cycloaddition reactions of diynes, enynes, and dienes have been scarcely investigated.[8]

Scheme 1



Recently, we have reported regioselective allylmanganation of homopropargylic alcohol derivatives with triallylmanganate.[9] In this communication, we wish to report our initial studies on the intramolecular cycloaddition reactions of diynes with triallylmanganate[10] which provide bicyclized products containing a seven-membered ring. This organomanganate-complex-assisted cycloaddition reaction suggests the possibility of a new and unprecedented reactivity pattern for manganese reagents; part of the allylic group can also be used to construct the resulting bicyclized products in one pot, as shown in Schemes 1 and 2. Cyclizations of enyne and diene are also described.

A tetrahydrofuran (THF) solution of *N*,*N*-bis(2-nonynyl)benzylamine (**1a**; 1.0 mmol) was added to a THF solution of triallylmanganate, generated from $MnCl_2$

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(3) Review of zirconium-promoted cyclization: (a) Negishi, E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 5, p 1163. (b) Negishi, E.; Takahashi, T. *Acc. Chem. Res.* **1994**, *27*, 124. (c) Uesaka, N.; Saitoh, F.; Mori, M.; Shibasaki, M.; Okamura, K.; Pate, T. *J. Org. Chem.* **1994**, *59*, 5633. Zirconium-catalyzed carbomagnesation and cyclization in the presence of a Grignard reagent have been reported: (d) Dzhemilev, U. M.; Vostrikova, O. S. *J. Organomet. Chem.* **1985**, *285*, 43. (e) Takahashi, T.; Seki, T.; Nitto, Y.; Saburi, M.; Rousset, C. J.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 6266. (f) Knight, K. S.; Waymouth, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 6268. (g) Visser, M. S.; Heron, N. M.; Didiuk, M. T.; Sagal, J. F.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1996**, *118*, 4291. Titanium-promoted cyclization: (h) Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6422. (i) Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788. (j) RajanBabu, T. V.; Nugent, W. A.; Taber, D. F.; Fagan, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 7128. (k) Grossman, R. B.; Buchwald, S. L. *J. Org. Chem.* **1992**, *57*, 5803. (l) Suzuki, K.; Urabe, H.; Sato, F. *J. Am. Chem. Soc.* **1996**, *118*, 8729. (m) Urabe, H.; Hata, T.; Sato, F. *Tetrahedron Lett.* **1995**, *36*, 4261. (n) Urabe, H.; Takeda, T.; Sato, F. *Tetrahedron Lett.* **1996**, *37*, 1253. (o) Urabe, H.; Sato, F. *J. Org. Chem.* **1996**, *61*, 6756. Titanium-catalyzed reaction: (p) Berk, S. C.; Grossman, R. B.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 8593. (q) Hicks, F. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 11688.

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(5) Trost, B. M.; Lee, D. C. *J. Am. Chem. Soc.* **1988**, *110*, 7255.

(6) Schore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 5, p 1037.

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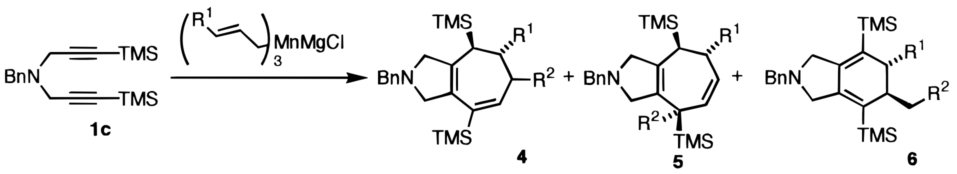
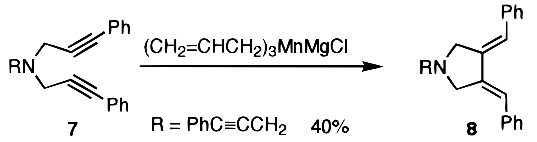
Scheme 2



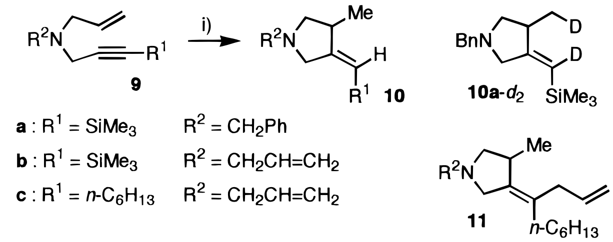
R^1 = H	R^2 = H	**4a** : 20%[a]	**5a** : 25%	**6a** : 25%
R^1 = Me	R^2 = H	**4b** : 12%[a]	**5b** : 13%	**6b** : 30%
R^1 = Me	R^2 = D	**4c** : 10%	**5c** : 10%	**6c** : 38%
R^1 = *n*-$C_{10}H_{21}$	R^2 = H	**4d** : 15%[a]	**5d** : 15%	**6d** : 36%

a : ref 11

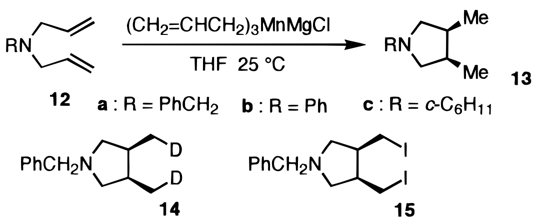
Scheme 3



Scheme 4



Scheme 5



(1.5 mmol) and allylmagnesium chloride (4.5 mmol) at 0 °C. The resulting mixture was stirred for 3 h at 0 °C. Extractive workup followed by silica gel column purification provided a mixture of 9-benzyl-2,6-dihexyl-9-azabicyclo[5.3.0]deca-1(7),2-diene (**2a**) and 9-benzyl-2,6-dihexyl-9-azabicyclo[5.3.0]deca-1(7),3-diene (**3a**) in 65% combined yield (**2a**:**3a** = 46:54).[11] *N*,*N*-Bis(2-butynyl)-benzylamine (**1b**) also gave the corresponding mixture of **2b** and **3b** (53% combined yield, **2b**:**3b** = 47:53) (Scheme 1).

The use of *N*,*N*-bis(3-(trimethylsilyl)-2-propynyl)benzylamine (**1c**) afforded 8-benzyl-3-methyl-2,5-bis(trimethylsilyl)-8-azabicyclo[4.3.0]nona-1,5-diene (**6a**) in addition to **4a** and **5a** in 70% combined yield (**4a:5a:6a** = 28:36:36). Treatment of **1c** with tricrotylmanganate instead of triallylmanganate afforded the corresponding mixture of 5-methylbicyclo[5.3.0]deca-1(7),2-diene (**4b**), 5-methylbicyclo[5.3.0]deca-1(7),3-diene (**5b**), and 3,4-dimethylbicyclo[4.3.0]nona-1,5-diene (**6b**), in 55% combined yield (**4b:5b:6b** = 22:24:54). Quenching the reaction intermediate with D_2O provided **4c**, **5c**, and **6c** in 10%, 10%, and 38% isolated yields, respectively.[12] Reaction with tris(2-tridecenyl)manganate also gave the corresponding mixture of **4d**, **5d**, and **6d** (Scheme 2).[13]

The terminal substituents of the diyne significantly affect the outcome of cyclization products. When the trimethylsilyl group was changed to a phenyl group, the reaction of **7** with triallylmanganate gave the product **8** instead of the bicyclization products (Scheme 3).

Next, the triallylmanganate-promoted cyclization reaction of enynes was studied. Treatment of *N*-allyl-*N*-benzyl-3-(trimethylsilyl)-2-propynylamine (**9a**) with triallylmanganate at 25 °C for 12 h provided cyclized product **10a** in 55% yield. Addition of D_2O to the reaction mixture, before quenching with MeOH, gave the corresponding dideuterated pyrrolidine derivative **10a**-d_2. In a similar fashion, *N*,*N*-diallyl-3-(trimethylsilyl)-2-propynylamine (**9b**) afforded **10b**. The use of *N*,*N*-diallyl-2-nonynylamine (**9c**) resulted in formation of a mixture of **10c** and allylated cyclized product **11** in a 1:1 ratio in 75% combined yield upon treatment with triallylmanganate (Scheme 4).

A diene such as *N*,*N*-diallylbenzylamine (**12a**) also provided a cyclized product, 1-benzyl-*cis*-3,4-dimethylpyrrolidine (**13a**),[14] as a single product in 70% yield. Quenching with D_2O or I_2 instead of H_2O provided the deuterated product **14** or diiodide **15** in 60% or 60% yield, respectively. *N*,*N*-Diallylaniline (**12b**) and *N*,*N*-diallylcyclohexylamine (**12c**) reacted with triallylmanganate as well as *N*,*N*-diallylbenzylamine (**12a**) and gave the corresponding pyrrolidine derivatives **13b** and **13c** in 70% and 70% yield, respectively (Scheme 5).

Although the mechanism has not yet been clarified, a possible mechanism may be envisaged as shown in Scheme 6. Reaction of **1** with triallylmanganate would provide the bicyclic manganacyclopentadiene **16**.[15] In the case of the reaction of **7** (R^1 = Ph, R^2 = $PhC{\equiv}CCH_2$) as a substrate, the intermediate **16** was quenched with water to give **8**. Meanwhile, the cyclopentadiene **16** derived from **1a** and **1b** could be converted into man-

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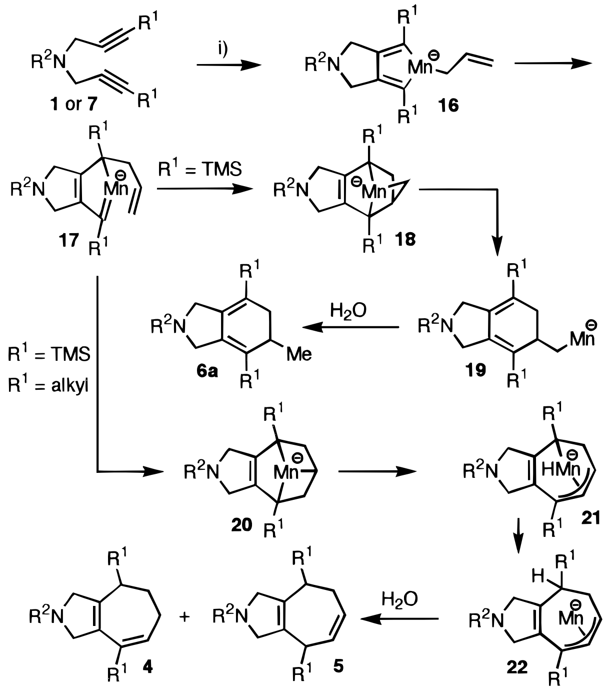
(11) The isolation of **2** and **4** in pure form was very difficult because of contamination by unidentified byproducts. Only **4c** could be separated by silica gel column chromatography in analytically pure form. Thus, the isolated yields of **2a**, **2b**, **4a**, **4b**, and **4d** were calculated using isolated yields of **3a**, **3b**, **5a**, **5b**, and **5d** based on the ratios determined by the examination of ^{1}H NMR of crude products. The details are described in the Supporting Information.

(12) A ^{1}H NMR examination of the crude product containing dibenzyl ether as an internal standard revealed that the yields and ratio of products were **4c** (16%), **5c** (16%), and **6c** (43%) (**4c**:**5c**:**6c** = 21:21:58), respectively.

(13) A mixture of three isomeric dienes, 3,4-decyl-1,5-hexadiene, 3-decyl-1,5-hexadecadiene, and 11,15-hexacosadiene (6:6:1) was isolated in 80% combined yield in addition to **4d**, **5d**, and **6d**.

(14) We thank Prof. M. Mori for sending us ^{1}H and ^{13}C NMR data for 1-benzyl-*cis*-3,4-dimethylpyrrolidine (**11a**) and its *trans* isomer: Yamaura, Y.; Hyakutake, M.; Mori, M. *J. Am. Chem. Soc.* **1997**, *119*, 7615.

Scheme 6



ganese carbene complex **17** by allyl migration from the manganese to an adjacent carbon. The reaction of the carbene complex with C═C intramolecularly would give the two manganacyclobutane intermediates **18** (R^1 = TMS, R^2 = $PhCH_2$) and **20** (R^1 = alkyl and TMS, R^2 = $PhCH_2$). The metallacyclobutane **18** may be transformed into the alkylmanganese species **19** via reductive elimination. Quenching with H_2O would give **6a**. Meantime, the other metallacyclobutane **20** may collapse to allyl complex **21** via β-hydride elimination and subsequent reductive elimination. An addition of H_2O would provide bicyclo[5.3.0] products **4** and **5** by protonation of the allylic moiety.

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Supporting Information Available: Text giving experimental procedures and compound characterization data (8 pages). Ordering information is given on any current masthead page.

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(15) The coordination of diynes, enynes, or dienes to triallylmanganate would give a low-valent manganese species with the departure of 1,5-hexadiene (see ref 12). The low-valent Mn(0) species undergoes oxidative coupling with diynes to provide bicyclic manganacyclopentadiene **16**.

(16) A reviewer offered us an alternative mechanism as follows. (1) Insertion of the allylic double bond gives **I**. (2) Insertion of the alkyne into the vinyl−Mn bond would afford **II**, which could be converted into **19** or **III** by reductive elimination. (3) β-Hydride elimination from **III** could give **IV**, which would isomerize to **21** via **V**.