

Communications

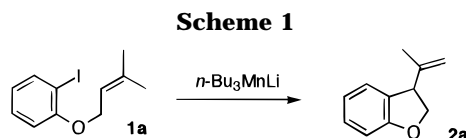
Trialkylmanganate-Induced Cyclization of Allyl 2-Iodophenyl Ether, *N,N*-Diallyl-2-iodoaniline, and α -Iodo Acetal

Junko Nakao, Rie Inoue, Hiroshi Shinokubo, and Koichiro Oshima*

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-01, Japan

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Dialkylcuprates¹ and trialkylzincates² have been widely used for organic synthesis. In contrast, much less information is available on the potential utility of trialkylmanganates.³ Herein, we report an effective method for the preparation of indoline, dihydrobenzofuran, and 2-alkoxytetrahydrofuran derivatives by means of tributylmanganate. Very recently, a synthesis of substituted indolines via anionic cyclization has been reported.⁴ In addition, several procedures mediated by free radical,⁵ transition metal species,⁶ and samarium(II) iodide⁷ have also been published on the construction of the heteroatom



ring of these molecules. Our new method should provide an alternative route to these important compounds.

A THF suspension of manganese(II) chloride (0.19 g, 1.5 mmol) was sonicated for 20 min under argon atmosphere. The mixture was cooled to 0 °C, and butyllithium (1.5 M hexane solution, 3.0 mL, 4.5 mmol) was added. After the mixture was stirred for 20 min, a solution of 2-iodophenyl prenyl ether (**1a**, 0.29 g, 1.0 mmol) in THF (2 mL) was added. The resulting mixture was stirred for 2 h and poured into 1 N HCl (20 mL). Extraction with hexane (20 mL \times 3) followed by silica gel column chromatography afforded 3-isopropenyl-2,3-dihydrobenzofuran (**2a**, 0.16 g) in 88% yield (Scheme 1). The use of tributylmanganate (*n*-Bu₃MnMgBr), derived from MnCl₂ and 3 equiv of butylmagnesium bromide, instead of *n*-Bu₃MnLi also provided **2a** in 87% yield. In contrast, *n*-Bu₂Mn, *n*-BuMnCl, Me₃MnLi, or *n*-Bu₂CuLi could not give any cyclized product.⁸

Representative examples are shown in Table 1. Not only 2-iodophenol derivatives **1** but also 2-iodoaniline derivatives **3** reacted in the same way to provide the corresponding indoline derivatives upon treatment with tributylmanganate. Several comments are worth noting. (1) Tributylmanganate magnesium bromide, *n*-Bu₃MnMgBr, was as equally effective as *n*-Bu₃MnLi. (2) The corresponding bromo compound such as 2-bromophenyl prenyl ether afforded phenyl prenyl ether (40%) along with the starting material (52%) upon treatment with tributylmanganate. (3) An addition of a THF solution of *n*-Bu₂Mn to 2-lithiophenyl propenyl ether, generated from **1a** and *n*-BuLi in THF, gave a complex mixture that did not contain the cyclized product **2a**. (4) The reaction of 2-iodophenyl homoallyl ether **1e** with tributylmanganate provided chroman derivative **2e** in only 30% yield. (5) The relative stereochemistry between the substituents attached to C(2) and C(3) of compound **2d** was *trans/cis* = 85/15. This isomeric ratio was the same as that of the radical cyclization product, 3-ethyl-2-methyl-2,3-dihydrobenzofuran (*trans/cis* = 87/13), which was generated by the reaction of **1d** with *n*-Bu₃SnH.

The intermediacy of the radical species was confirmed by the following experiment. Treatment of allylic ether **1f** having a cyclopropane ring on the alkenyl carbon with tributylmanganate provided a mixture of dienyl-substituted dihydrobenzofuran derivative **2f** and alkenyl-substituted compound **2f'** (**2f**:**2f'** = 2:1) in 52% combined yield (Scheme 2). No trace of the product having the cyclopropane ring could be observed in the reaction mixture.⁹

The intermediary manganese species could be trapped

(8) Treatment of **1a** with *n*-Bu₂Mn and *n*-BuMnCl resulted in recovery of the starting ether **1a**. The reaction with Me₃MnLi provided phenyl prenyl ether quantitatively. *n*-Bu₂CuLi afforded the starting material **1a** (60%) and phenyl prenyl ether (35%). In addition, treatment of **1a** with *n*-BuLi gave phenyl prenyl ether exclusively after aqueous workup.

(9) Fossey, J.; Lefort, D.; Sorba, J. *Free Radicals in Organic Chemistry*; John Wiley & Sons: Chichester, 1995; p 159.

(1) (a) Taylor, R. J. K., Ed.; *Organocopper Reagents A Practical Approach*; Oxford University Press: Oxford, 1994. (b) Lipshutz, B. H.; Sengupta, S. *Org. React.* **1992**, *41*, 135. (c) Lipshutz, B. H. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 1, Chapter 1.4, 107. (d) Lipshutz, B. H. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; Wiley: New York, 1994. (e) Yamamoto, Y. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 947. (f) Nakamura, E. *Synlett* **1991**, 539. (g) Knochel, P.; Singer, R. D. *Chem. Rev.* **1993**, *93*, 2117.

(2) (a) Isobe, M.; Kondo, S.; Nagasawa, N.; Goto, T. *Chem. Lett.* **1977**, 679. (b) Seebach, D.; Langer, W. *Helv. Chim. Acta* **1979**, *62*, 1701, 1710. (c) Harada, T.; Katsuhira, T.; Hattori, K.; Oku, A. *J. Org. Chem.* **1993**, *58*, 2958. (d) Harada, T.; Wada, H.; Oku, A. *J. Org. Chem.* **1995**, *60*, 5370.

(3) (a) Cahiez, G. *Butyl Manganese Chloride and Related Reagents in Encyclopedia of Reagents for Organic Synthesis*; Paquette, L., Ed.; Wiley: Chichester, **1995**; p 925. (b) Cahiez, G. *Manganese(II) Chloride in Encyclopedia of Reagents for Organic Synthesis*; Paquette, L., Ed.; Wiley: Chichester, 1995; p 3227. (c) Cahiez, G. *An. Chim.* **1995**, *91*, 561. (d) Corey, E. J.; Posner, G. H. *Tetrahedron Lett.* **1970**, 315. (e) Okada, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc.* **1996**, *118*, 6076. (f) Inoue, R.; Shinokubo, H.; Oshima, K. *Tetrahedron Lett.* **1996**, *37*, 5377. Decomposition of the dialkylmanganese species has been reported. Tamura, M.; Kochi, J. *J. Organomet. Chem.* **1971**, *29*, 111.

(4) (a) Zhang, D.; Liebeskind, L. S. *J. Org. Chem.* **1996**, *61*, 2594. (b) Bailey, W. F.; Jiang, X.-L. *J. Org. Chem.* **1996**, *61*, 2596. (c) Uchiyama, M.; Koike, M.; Kameda, M.; Kondo, Y.; Sakamoto, T. *J. Am. Chem. Soc.* **1996**, *118*, 8733.

(5) (a) Sloan, C. P.; Cuevas, J. C.; Quesnelle, C.; Snieckus, V. *Tetrahedron Lett.* **1988**, *29*, 4685. (b) Wolff, S.; Hoffmann, H. M. R. *Synthesis* **1988**, 760. (c) Boger, D. L.; Palanki, M. S. S. *J. Am. Chem. Soc.* **1992**, *114*, 9318. (d) Rao, A. V. R.; Gurjar, M. K.; Bose, D. S.; Devi, R. R. *J. Org. Chem.* **1991**, *56*, 1320. (e) Boger, D. L.; Yun, W.; Teegarden, B. R. *J. Org. Chem.* **1992**, *57*, 2873. (f) Clive, D. L. J.; Etkin, N.; Joseph, T.; Lown, J. W. *J. Org. Chem.* **1993**, *58*, 2442. (g) Boisvert, G.; Giasson, R. *Tetrahedron Lett.* **1992**, *33*, 6587. (h) Rai, R.; Collum, D. B. *Tetrahedron Lett.* **1994**, *35*, 6221. (i) Itoh, T.; Ohara, H.; Emoto, S. *Tetrahedron Lett.* **1995**, *36*, 3531.

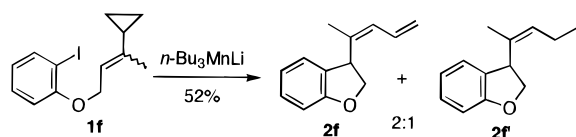
(6) (a) Iqbal, J.; Bhatia, B.; Nayyar, N. K. *Chem. Rev.* **1994**, *94*, 519. Palladium-catalyzed cyclization: Larock, R. C.; Stinn, D. E. *Tetrahedron Lett.* **1988**, *29*, 4687. Larock, R. C.; Babu, S. *Tetrahedron Lett.* **1987**, *28*, 5291. Larock, R. C.; Stinn, D. E. *Tetrahedron Lett.* **1989**, *30*, 2767. Hegedus, L. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1113. Sakamoto, T.; Kondo, Y.; Yamanaka, H. *Heterocycles* **1988**, *27*, 2225. Nickel: Mori, M.; Kudo, S.; Ban, Y. *J. Chem. Soc., Perkin Trans. 1* **1978**, 771. Olivero, S.; Clinet, J. C.; Dunach, E. *Tetrahedron Lett.* **1995**, *36*, 4429. Cobalt: Pattenden, G. *Chem. Soc. Rev.* **1988**, *17*, 361. Zn-Mn: Riguët, E.; Klement, I.; Reddy, C. K.; Cahiez, G.; Knochel, P. *Tetrahedron Lett.* **1996**, *37*, 5865. Zn-Ni: Vaupel, A.; Knochel, P. *J. Org. Chem.* **1996**, *61*, 5743.

(7) Curran, D. P.; Totleben, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 6050.

Table 1. Tributylmanganate-Induced Cyclization of Allyl 2-Iodophenyl Ethers and *N,N*-Diallyl-2-iodoaniline

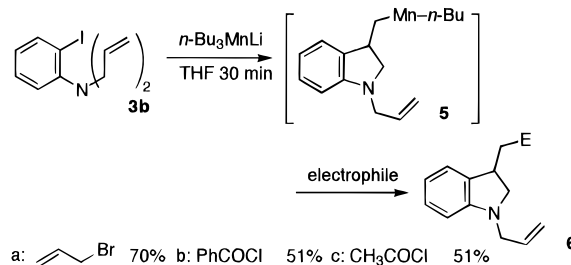
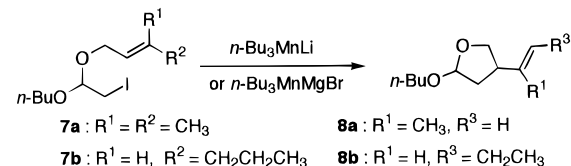
Entry	Substrate	Product	Yield (%)
1			40
2			63
3			70 ^b
4			30
5			92 (90) ^c
6			72 (72) ^c
7			74

^a *n*-Bu₃MnLi (1.5 mmol) and substrate (1.0 mmol) were employed. ^b *cis/trans* = 15/85. ^c *n*-Bu₃MnMgBr was used instead of *n*-Bu₃MnLi.

Scheme 2

by various electrophiles.¹⁰ An addition of tributylmanganate to diallylaniline derivative **3b** followed by treatment with allyl bromide provided the corresponding allylated product **6a** (E = CH₂CH=CH₂) in 70% yield. Trapping the reaction by acid chlorides such as acetyl chloride and benzoyl chloride afforded methyl ketone and phenyl ketone, respectively (Scheme 3).

Unexpectedly, the reaction proved to proceed in the

Scheme 3**Scheme 4**

presence of a catalytic amount of manganese chloride.¹¹ For instance, treatment of **1a** (1.0 mmol) or **3a** (1.0 mmol) with excess *n*-BuMgBr (4.0 mmol) in the presence of a catalytic amount of MnCl₂ (0.2 mmol) in THF at 25 °C for 12 h provided **2a** or **4a** in 70% or 81% yield, respectively. The reactions were performed in a flask equipped with a balloon filled with argon. Atmospheric oxygen could diffuse into the balloon to equilibrate the partial pressures, and the concentration of oxygen reached 10% (volume %) after 12 h.¹² The presence of oxygen was essential for the catalytic reaction.^{3c} Without oxygen, the cyclization reaction did not complete under MnCl₂ catalysis.

The radical cyclization reaction of unsaturated iodo acetals **7a** and **7b** was examined.¹³ Treatment of **7a** or **7b** with *n*-Bu₃MnLi provided **8a** or **8b** in 82% or 73% yield (Scheme 4). The catalytic reaction (10 mol % MnCl₂) using *n*-BuMgBr (2.0 mmol) could also be applied to iodo acetal **7a** (1.0 mmol) to give **8a** in 80% yield, in which case the presence of oxygen was not necessary.¹⁴

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Supporting Information Available: Experimental procedures and compound characterization data (6 pages).

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(10) Examples of sequences: (1) radical cyclization, (2) reduction to an organometallic, and (3) electrophilic tapping: (a) Nugent, W. A.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1988**, *110*, 8561. (b) Takai, K.; Nitta, K.; Fujimura, O.; Utimoto, K. *J. Org. Chem.* **1989**, *54*, 4732. (c) See ref 7.

(11) Anionic cyclization of **3** with *t*-BuLi has been reported.⁴ However, an addition of a Grignard reagent (*n*-BuMgBr) to **1a** or **3a** in the absence of MnCl₂ afforded only the reduced product, phenyl prenyl ether, or *N,N*-diprenylaniline in 20% or 30% yield along with the recovered starting materials.

(12) The catalytic reaction also proceeded in the atmosphere. Stirring a mixture of **3a** (1.0 mmol), *n*-BuMgBr (4.0 mmol), and MnCl₂ (0.1 mmol) or MnCl₂ (0.3 mmol) in the atmosphere afforded **4a** in 60% or 80% yield, respectively, along with the recovered starting material **3a** in 30% or 14% yield. The reaction in a flask under argon balloon gave a better yield of **3a** than the reaction in the atmosphere. Thus, slow injection of oxygen might be essential for the catalytic reaction.

(13) The corresponding bromo acetal BrCH₂CH(O-*n*-Bu)OCH₂-CH=CMe₂ provided **8a** in 41% yield under the same reaction conditions.

(14) The catalytic reaction was complete in 3 h at 0 °C under argon atmosphere in a sealed system.