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Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsyc20</u>

A Mild and Efficient Oxidation of Alcohols to Ketones with Iodosobenzene/(Salen) Manganese Complex

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Version of record first published: 19 Aug 2006.

To cite this article: Sung Soo Kim# & Galina Borisova (2003): A Mild and Efficient Oxidation of Alcohols to Ketones with Iodosobenzene/(Salen) Manganese Complex, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 33:22, 3961-3967

To link to this article: http://dx.doi.org/10.1081/SCC-120026321

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SYNTHETIC COMMUNICATIONS[®] Vol. 33, No. 22, pp. 3961–3967, 2003

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ABSTRACT

An excellent method for the chemoselective oxidation of alcohols to ketones with C_6H_5IO catalyzed by (salen) manganese/4Å MS in CH₃CN has been devised. The reported procedure is fast, simple, and the yields are excellent (>95%) in most cases.

Key Words: Alcohol; Ketone; Chemoselective; Mn(salen); Iodosobenzene.

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DOI: 10.1081/SCC-120026321 Copyright © 2003 by Marcel Dekker, Inc. 0039-7911 (Print); 1532-2432 (Online) www.dekker.com

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[#]This article was written during the sabbatical leave of absence.

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INTRODUCTION

The oxidation of alcohols to aldehydes and ketones is one of the most important transformations in organic synthesis.^[1] The achiral chromium(III)^[2] and manganese(III)^[3] complexes of the salen ligand are the effective catalysts for the epoxidation of various olefins with iodosobenzene as the terminal oxidant. Chiral (salen) manganese catalysts^[4,5] were combined with iodosylbenzene, sodium hypochlorite, or *m*-chloroperbenzoic acid for the enantioselective epoxidation of *cis*- and *trans*-substituted olefins.

E-β-methylstyrene, a *trans*-olefin^[6] undergo asymmetric epoxidation utilizing (salen) chromium complex/iodosobenzene with triphenylphosphine oxide as the additive. The alcohols^[7] were oxidized into aldehydes and ketones with the hypervalent iodine(III) reagents triggered by various catalysts. (Salen) chromium(III) catalyzed oxidations of a series of allylic and benzylic alcohols to corresponding carbonyl compounds^[8,9] have been carried out with either iodosobenzene or iodosobenzene diacetate as the oxidant. We now report the oxidation of these alcohols with a new (salen) manganese complex.

RESULTS AND DISCUSSION

N,N'-bis(3,5-dichlorosalicylidine)-1,2-ethylenediaminomanganese(III) chloride(I) was synthesized according to the known procedure.^[8,10] Catalyst I is used with C₆H₅IO as an oxidant under various conditions for the oxidation of 1-phenylethanol (Table 1).

Comparison of result of entries 1 and 2 indicate that addition of 4 Å molecular sieve (MS) improves yield of the ketone. CH₃CN appears to be the best solvent for the oxidation (entries 1, 3–5). Accordingly the



Figure 1. I:N,N'-*bis*(3,5-Dichlorosalicylidene)-1,2-ethylenediaminomanganese (III) chloride (C₁₆H₁₀Cl₅N₂O₂Mn; M.W. 494.47).

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Table 1. Oxidation of 1-phenylethanol with C_6H_5IO at r.t. under various conditions.^a

Entry	Catalyst	Additive	Solvent	Time (h)	Yield (%)
1	Ι	4Å MS	CH ₃ CN	2	89
2	Ι		CH ₃ CN	2	82
3	Ι	4Å MS	C_6H_6	4	58
4	Ι	4Å MS	CH_2Cl_2	4	40
5	Ι	4Å MS	EtOAc	4	62

^aCatalyst:C₆H₆IO:additive:solvent = 0.1 mmol: 1.5 mmol: 0.12 g: 4 mL.



factors of entry 1 of Table 1 constitute most favorable conditions for the oxidation. The mechanism of oxidative process is indicated in Sch. 1.

1-Phenylethanols containing substituents on phenyl ring (entries 1–6) (Table 2) are efficiently oxidized to corresponding ketones for relatively short reaction time. The reactions show little substituent effect on the oxidative process. The change of methyl of 1-phenylethanol to other larger groups (entries 7–11) hardly influences the reactivity and also the yield. Only entry 12 gives a little lower yield. Therefore, most of secondary benzylic alcohols indicate vigorous reactivity towards oxidation within relatively short reaction time (yield: 89–99%, reaction time: 1–2 h). Similar secondary benzylic oxidation previously^[8] gave only satisfactory results (yield: 20–69%, reaction time: 14 h). On the contrary, primary benzylic alcohol (entry 13) takes longer time for the oxidation to give only poor yield. The reluctance of the reaction has been also observed for oxidation of allylic alcohol (entry 14).

Present catalytic system is useful for the oxidation of secondary benzylic alcohols to ketones. However benzylic and allylic alcohols reveal poor oxidative tendency. ©2003 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

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	ŎН	C ₆ H ₅ IO / [Mn(III)(salen)Cl]	Q	
	Ph—C—R	4\AA MS , CH_3CN , r.t.	→ PhC-	-R
Substrate 1 mmol	C ₆ H₅IO 1.5 mmol	[Mn(III)(salen)Cl] 0.1 mmol	4Å MS 0.12 g	CH ₃ CN 4 mL
Entry	Substrate	Product	Time (h)	Yield ^{a,b} (%)
1	OH	, i	2	89
2	OH Me	Me	2	86
3	ОН Мео	MeO	2	95
4	Br	Br	2	97
5	CI	c	2	97
6	CI OH	CI	1	99
7	OH		2	99
8	ОН		1	92
9	ОН		1.5	99
10	ОН		1.5	99

<i>Table 2.</i> Oxidation of alcohols with $[Mn(III)(salen)Cl]/C_6H_5IO$ at r.

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Iodosobenzene/(Salen)	Manganese Complex	
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Table 2. Continued.	
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Entry	Substrate	Product	Time (h)	Yield (%) ^{a,t}
11 ^c	ОН	Å	1	89
12	ОН		1	77
13	ОН		18	11
14	ОН		6	67

^aIsolated yield.

^bAll the ¹H NMR spectra of ketones and aldehydes exactly match with those tabulated in the aldrich library of ¹³C and ¹H FT NMR spectra by edited Charles J. Pouchert, Jacqlynn Behnke.

 $^{c}N,N-bis(5-$ Chlorosalicylidine) - 1,2 ethylenediaminomanganese(III) chloride. (C₁₆H₁₂Cl₃N₂O₂Mn; M.W. 425.57) is the catalyst for the oxidation.

EXPERIMENTAL

N,*N'-bis*(3,5-Dichlorosalicylidine)-1,2ethylenediaminomanganese(III) Chloride

Ethylenediamine (0.300 g, 5 mmol) was added to solution of 3,5-dichlorosalicylaldehyde (1.91 g, 10 mmol) in anhydrous ethanol (30 mL) in a round-bottom flask equipped with a magnetic bar and West condenser. The yellow solution was refluxed for 3 h. The reaction mixture was then allowed to react overnight at ambient temperature. The mixture was filtered to yield clean *bis*-(3,5-dichlorosalicylidene)-ethylene-diamine. (Yield: 1.9 g, 94%). ¹H NMR (CDCl₃): δ 4.01 (s, 4H, (CH₂)₂), 7.16 (d, 2H, C₆H₂), 7.90 (d, 2H, C₆H₂), 8.28 (s, 2H, (CH)₂).

To a suspension of bis-(3,5-dichlorosalicylidene)ethylenediamine [0.609 g (1.5 mmol)] in absolute ethanol (30 mL) was added suspension of Mn(OAc)₂·4H₂O [0.367 g (1.5 mmol)] in ethanol (30 mL) which were allowed to reflux in the air for 3 h. Then 3-M-fold quantity of lithium chloride was added to this solution and was further refluxed for 1 h. The reaction mixture was left overnight at r.t. and filtered. The filtrate was dried under reduced pressure to afford 0.69 g of the required complex,

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I (yield: 93%). Anal. calcd. for $C_{16}H_{10}Cl_5N_2O_2$ Mn: C, 38.86; H, 2.03; N, 5.66. Found: C, 38.54; H, 2.32; N, 5.92.

General Procedure for the Oxidation of the Alcohols with PhIO Catalyzed by I

To a solution of the substrate (1.00 mmol) in CH₃CN (4 mL) was added 0.1 equiv. of catalyst I, 0.12g of 4 Å MS and 1.5 equiv. of iodosobenzene. The mixture was stirred for hours and the solvent was evaporated. The remainder was subject to silica gel column chromatography with ethyl acetate:hexane (2:8) mixture as eluent. The solvent was removed by evaporation and the products were identified by ¹H NMR spectroscopy.

ACKNOWLEDGMENT

The authors warmly thank Korea Science and Engineering Foundation for the financial support (R01-2001-00057). G. Borisova has been supported by the fund from KISTEP.

REFERENCES

- Larock, R.C. Comprehensive Organic Transformations, 2nd Ed.; John Wiley & Sons: New York, 1999.
- Samsel, E.G.; Srinivasan, K.; Kochi, J.K. J. Am. Chem. Soc. 1985, 107, 7606–7617.
- Srinivasan, K.; Michaud, P.; Kochi, J.K. J. Am. Chem. Soc. 1986, 108, 2309–2320.
- (a) Zhang, W.; Loebach, J.C.; Wilson, S.R.; Jacobsen, E.N. J. Am. Chem. Soc. 1990, 112, 2801–2803; (b) Jacobsen, E.N.; Zhang, W.; Much, A.; Ecker, J.R.; Deng, L. J. Am. Chem. Soc. 1991, 113, 7063–7064; (c) Chang, S.; Galvin, J.M.; Jacobsen, E.N. J. Am. Chem. Soc. 1994, 116, 6937–6938; (d) Brandes, B.D.; Jacobsen, E.N. J. Org. Chem. 1994, 59, 4378–4380.
- (a) Irie, R.; Noda, K.; Ito, Y.; Matsumoto, N.; Katsuki, T. Tetrahedron Lett. **1990**, *31*, 7345–7348; (b) Irie, R.; Ito, Y.; Katsuki, T. Synlett **1991**, 265–266; (c) Hamada, T.; Irie, R.; Katsuki, T. Synlett **1994**, 479–481; (d) Sun, W.; Wang, H.; Xia, C.; Li, J.; Zhao, P. Angew. Chem. Int. Ed. **2003**, *42*, 1042–1044.

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- (a) O'Mahony, C.P.; McGarrigle, E.M.; Renehan, M.F.; Ryan, K.M.; Kerrigan, N.J.; Bousquet, C.; Gilheany, D.G. Org. Lett. 2001, 3, 3435–3438; (b) Ryan, K.M.; Bousquet, C.; Gilheany, D.G. Tetrahedron Lett. 1999, 40, 3613–3616.
- (a) Utimoto, K.; Oshima, K.; Matsumoto, K.; Yokoo, T. Chemister Lett. **1993**, 571–572; (b) Kita, Y.; Tohma, H.; Takizawa, S.; Maegawa, T. Angew. Chem. Int. Ed. **2000**, *39*, 1306–1308; (c) Nishiyama, H.; Iwasa, S.; Morita, T.; Fakhruddin, A. Chem. Lett. **2002**, 284–285.
- Adam, W.; Gelalcha, F.G.; Saha-Möller, C.R.; Stegmann, V.R. J. Org. Chem. 2000, 65, 1915–1918.
- Adam, W.; Hajra, S.; Herderich, M.; Saha-Möller, C.R. Org. Lett. 2000, 2, 2773–2776.
- Larrow, J.F.; Jacobsen, E.N.; Gao, Y.; Hong, Y.; Nie, X.; Zepp, C.M. J. Org. Chem. 1994, 59, 1939–1942.

Received in Japan May 12, 2003



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