Mn-Catalyzed Reductive Cleavage of Aromatic Carbon-Oxygen Bonds

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Abstract：Manganese compounds were found to be effective to catalyze the reductive cleavage of carbon-oxygen bonds. To the best of our knowledge，no effective Mn-based catalyst was reported for this process. The reaction conditions were optimized by choosing dibenzofuran as the substrate，and the obtained optimum conditions were as follows：5% Mn(OAc)$_2$，3 equiv. LiAlH$_4$，140 ℃ as the reaction temperature，THF as the solvent. The optimum conditions allowed a series of aromatic carbon-oxygen bonds to undergo the reductive cleavage. An addition of sodium methoxide was beneficial for the reaction of some substrates including diphenyl ethers. Preliminary mechanistic investigation suggests that the present reaction possibly undergoes a radical pathway.

Key words：reductive cleavage；carbon-oxygen bond；manganese；catalysis

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The selective cleavage of aromatic carbon-oxygen bonds is a considerably challenging process[1-2] in the organic transformations related to the readily available phenolic derivatives[3-4]. In addition，this process is important for the conversion of lignin into small molecules that can be further converted into fuels or high value chemicals[5-9]. As a result，much effort has been devoted to developing various methods for the selective cleavage of the aromatic carbon-oxygen bonds under the catalysis of Ni[10-14]，Pd[15-16]，Co[17]，Fe[18-19]，Rh[20-21] and Ir[22] compounds. However，to the best of our knowledge，no effective Mn-based catalyst has been reported for this process. Thus our interest has been focused on an investigation on the catalysis of the Mn compounds with the reductive cleavage as the model reaction.

In 2010，Martin and co-workers described a highly selective example for the reductive cleavage of the aromatic carbon-oxygen bonds with tetramethyldisiloxane as the hydride source under the catalysis of Ni compound[23]. Subsequently，the nickel based catalysts stabilized by a *N*-heterocyclic carbene were designed to catalyze the selective reductive cleavage with hydrogen gas[24-25]. Recently，several heterogeneous Ni-catalyst systems were found to be effective for the cleavage with hydrogen gas[26-27]. In 2013，a Rh/C catalyzed method in the scCO$_2$/water medium was developed by the Chatterjee group[28]. In 2015，the Nozaki group reported iridium-catalyzed selective hydrogenolysis of arenols and aryl methyl ethers[22]. Besides the above-mentioned hydrogen gas and hydrosilanes[29]，LiAlH$_4$ was also found to be effective as the hydride source for the reductive cleavage[30]. We have launched an investigation to use readily available LiAlH$_4$ as the hydride do-

nor for the reductive cleavage under the catalysis of the Fe compounds[30]. Similar results were obtained by us in the case of using a cobalt-based catalyst system[17]. In 2015, Liu and co-workers reported the reductive cleavage of various phenolic compounds and aryl ethers using LiAlH$_4$ and t-BuOK in the absence of the transition metals[31]. In the present paper, we report a Mn-based catalyst for the selective reductive cleavage of aromatic C—O bonds with LiAlH$_4$ as the hydride donor.

1 Experimental

1.1 Materials and instruments

The quality and suppliers of the chemicals are listed in Table S1. All substituted diphenyl ethers were synthesized by the reaction between the corresponding substituted iodobenzenes and substituted phenols[26]. The other chemicals were obtained from commercial vendors and used without further purification.

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker 500 MHz instrument with chemical shifts reported in ppm relative to the internal standard tetramethylsilane. Gas chromatography analyses were performed on a Varian CP-3800 instrument with a FID detector and a CP-WAX 57CB FS capillary chromatographic column (25 m × 0.32 mm). GC-MS spectra was recorded on an Agilent 6890/5973N gas chromatography-mass spectrometry instrument.

1.2 General procedure for the reductive cleavage

0.5 mmol substrate, 1.5 mmol LiAlH$_4$, 0.025 mmol Mn(OAc)$_2$ and 2 mL dry THF were added to a dried 45 mL tube equipped with a magnetic stirrer. Then the reaction tube was sealed and placed in a constant-temperature groove to perform the reaction for 20 h. Once the reaction time was reached, the mixture was cooled to room temperature. The mixture was then acidified to pH 5 ~ 6 with 2 mol/L hydrochloric acid. GC analysis of the mixture provided the yields of the products (note: in order to minimize the analytical error, the mixture after the reaction was not purified or concentrated). The reductive cleavage products were identified by GC-MS. Some products were purified by column chromatography, and identified by ^{13}C-NMR.

2 Results and discussion

Dibenzofuran was chosen as the substrate to start our investigation by using 5% Mn(OAc)$_2$ as the catalyst, 3 equiv. LiAlH$_4$ as the reducing agent, and THF as the reaction solvent at 140 ℃. The reductive cleavage did not occur in the absence of Mn(OAc)$_2$, while an addition of 5% Mn(OAc)$_2$ allowed the targeted biphenyl-2-ol product to be obtained in 63% yield (Table 1, entries 2 and 3), and hardly any other product was observed. These results revealed that the catalytic amount of Mn compound played a critical role in the reaction. An increase of the loading amount of Mn(OAc)$_2$ or LiAlH$_4$ possibly allowed the reductive cleavage to proceed in high yield, but the resulting experimental results were less reproducible. When 3 equiv. CH$_3$ONa was added to the reaction system, the yield of the targeted product increased from 63% to 93% (Table 1, entry 4), which suggested that the addition of CH$_3$ONa was beneficial for the reaction. We tried to decrease the reaction temperature to 120 ℃ or 100 ℃ from 140 ℃, but found that this was not possible without sacrificing product yield even if the reaction time was prolonged to 40 h (Table 1, entries 5 and 6). Among the screened bases, CH$_3$ONa and t-BuONa turned out to be the most effective two (Table 1, entries 4 and 7), while the reactions with Mg(EtO)$_2$, t-BuOLi and MeOLi provided the desired product in moderate yields (Table 1, entries 8-10). The solvent had a vital effect on the reaction: although the reaction using tetrahydrofuran proceeded smoothly, other solvents including cyclohexane, toluene and trimethylbenzene were less effective (Table 1, entries 11-13). This phenomenon was not consistent with the results from Co or Fe-catalyzed reductive cleavage of aromatic C—O bonds with LiAlH$_4$ as the reducing agent reported in previous literatures[17,30] where toluene was the most effective solvent. As shown in Table 1 (entries 14-17), Mn(OAc)$_2$ was the most effective catalyst. When Mn(OAc)$_2$ was replaced by MnCl$_2$, only 18% yield of the targeted product was obtained. The reaction with manganese(II) acetyllacetonate and manganese(II) oxalate gave the product in respectively 56% and 53% yield.
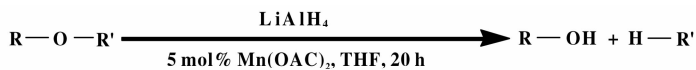
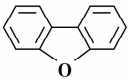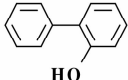**Table 1 Reductive cleavage of aromatic C-O bonds in dibenzofuran catalyzed by Mn(OAc)₂ᵃ**
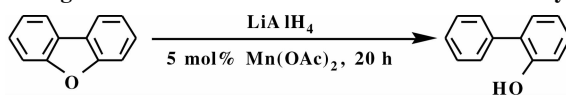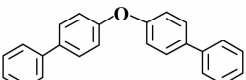
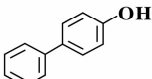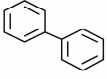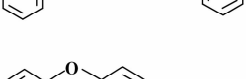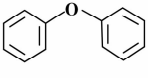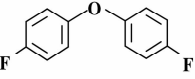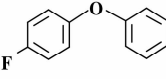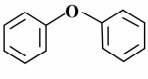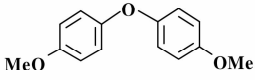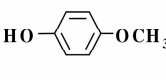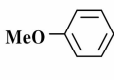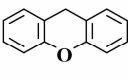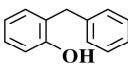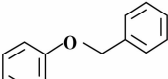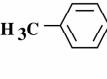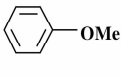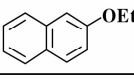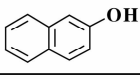| Entry	Temperature/℃	Solvent	Base	Yield/(%)[b]
1	120	THF	–	trace
2	140	THF	–	63
3[c]	140	THF	–	trace
4	140	THF	MeONa	93
5	120	THF	MeONa	82
6	100	THF	MeONa	30
7	140	THF	t-BuONa	95
8	140	THF	Mg(EtO)₂	74
9	140	THF	t-BuOLi	83
10	140	THF	MeOLi	82
11	140	cyclohexane	MeONa	trace
12	140	toluene	MeONa	trace
13	140	trimethylbenzene	MeONa	trace
14[d]	140	THF	–	18
15[d]	140	THF	–	23
16[d]	140	THF	–	56
17[d]	140	THF	–	53

a. Reaction conditions: dibenzofuran (0.5 mmol), LiAlH₄(1.5 mmol), base (1.5 mmol), Mn(OAc)₂(0.025 mmol), solvent (2 mL), 20 h; b. etermined with an internal standard; c. No Mn(OAc)₂ was added; d. Mn(OAc)₂ is respectively replaced by MnCl₂(entry 14), MnSO₄(entry 15), manganese(II) acetyllacetonate (entry 16), manganese(II) oxalate (entry 17)

Subsequently, a variety of aromatic C—O bonds in various substrates were tested to determine the scope and limitation of the present protocol. As shown in Table 2, the aromatic C—O bonds in several substrates underwent this transformation smoothly under the base-free condition. For example, the reductive cleavage of 4,4′-diphenyldiphenyl ether gave 4-hydroxybiphenyl and biphenyl in 100% and 91% yields respectively (Table 2, entry 3), even a decrease of the reaction temperature to 100 ℃ did not lead to the decline of the yield (Table 2, entry 2). By comparison, the aromatic C—O bonds in the other diphenyl ethers gave lower conversions and yields under all the test conditions (Table 2, entries 4~6). Especially in the case of 4,4′-difluorodiphenyl ether (Table 2, entry 5), aromatic C—F bonds underwent the cleavage, and only small amount of products from the reductive cleavage of aromatic C—O bonds was observed. When 4,4′-dimethoxydiphenyl ether was used as the substrate, the reductive cleavage mainly occurred at the side of the diphenyl ether moiety, and the p-benzenediol and phenol products from the reductive cleavage of the anisole moiety were obtained in respectively 11% and 7% yield (Table 2, entry 6). Compared with diphenyl ether, 4,4′-dimethoxydiphenyl ether was cleaved to give the targeted products in higher yields (Table 2, entries 4 and 6), revealing that the electron-donating substituent groups bonded to the aromatic rings were beneficial for the reaction. Xanthene was also an excellent substrate, and was converted to the desired product in 98% yield in the case of 120 ℃ (Table 2, entry 8). When benzofuran was used as the substrate, the reductive cleavage selectively occurred at the vinyl C—O bond rather than the aromatic C—O bond, and the π-bond in the ethyleneoxy also underwent the cleavage. Methylene C—O bonds in benzyl phenyl ethers were well cleaved over the aromatic C—O bonds under our condition (Table 2, entries 13 and 14). When alkoxyl naphthalenes and alkoxyl benzenes were used as the substrates, the alkyl C—O bonds were selectively cleaved (Table 2, entries 15~18), which was different from the results of Fe or Co-catalyzed reductive cleavage reported in literatures[17,30] where only the products from the cleavage of aromatic C—O bonds were observed.

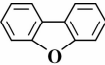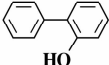**Table 2 Base-free reductive cleavage of various aromatic C-O bonds catalyzed by Mn(OAc)₂[a]**

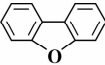$$R—O—R' \xrightarrow[\text{5 mol\% Mn(OAC)}_2\text{, THF, 20 h}]{\text{LiAlH}_4} R—OH + H—R'$$

Entry	Substrate	Temperature /℃	Product 1	Yield l/(%)[b]	Product 2	Yield (%)[b]
1	(dibenzofuran)	140	(2-hydroxybiphenyl)	63	–	–
2	(bis-phenyl phenyl ether)	100	(hydroxy-biphenyl)	85	(biphenyl)	~100
3		120		~100[c]		91[c]
4	(diphenyl ether)	140	(phenol)	18	(benzene)	20
5[d]	(bis-4-F-phenyl ether)	140	(4-F-phenyl phenyl ether)	24	(diphenyl ether)	71
6[e]	(bis-4-MeO-phenyl ether)	140	(HO—C₆H₄—OCH₃)	33	(MeO—phenyl)	40
7	(xanthene)	140	(2-hydroxydiphenylmethane)	96	–	–
8		120		98	–	–
9		100		76	–	–
10	(benzofuran)	140	(2-ethylphenol)	92	–	–
11		120		85	–	–
12		100		30	–	–
13	(benzyl phenyl ether)	140	(phenol)	86	(toluene, H₃C—)	105
14		120		81		96
15	(anisole, OMe)	140	(phenol)	43	–	–
16	(1-methoxynaphthalene)	140	(1-naphthol)	96[c]	(naphthalene)	1
17		120		93		1
18	(2-ethoxynaphthalene)	140	(2-naphthol)	94	(naphthalene)	–

a. Reaction conditions: Substrate (0.5 mmol), LiAlH₄(1.5 mmol), Mn(OAc)₂(0.025 mmol), THF (2 mL), 20 h; b. Determined with an internal standard; c. The isolated yields were respectively 81% and 76% (entry 3), 64% (entry 16); d. Beside of benzene(2% yield) and phenol(3% yield), no other product was observed; e. Conversion of the substrate is 52%, p-benzenediol and phenol were obtained in respectively 11% and 7% yield.

Considering that the reaction of aromatic carbon-oxygen bonds in some substrates did not proceed smoothly, we added CH_3ONa into the reaction system to overcome the limitation of the base-free method, and the results were shown in Table 3. An addition of CH_3ONa increased the yield of 2-phenyl phenol from

Table 3 Mn-catalyzed reductive cleavage of various aromatic C—O bonds in the presence of CH_3ONa^a

$$R-O-R' \xrightarrow[\text{5 mol\% Mn(OAc)}_2,\ \text{THF, 20 h}]{\text{LiAlH}_4,\ CH_3ONa} R-OH + H-R'$$

Entry	Substrate	Temperature /℃	Product 1	Yield /%[b]	Product 2	Yield /%[b]
1		120		76	–	–
2		140		93[d]	–	–
3		100		85		~100
4		140		34		70
5		120		24		87
6		140		75		14
7		120		63		4
8		140		82[d]		~100
9[c]		120		57		77
10[c,e]		100		52		31
11[e]		120		44		63
12		140		53		62
13		140		85		~100
14		140		66		66
15[c]		100		89[d]		93
16[c]		100		71		–
17		120		92		3
18[c]		100		70		–
19		120		88		1

a. Reaction conditions：Substrate（0.5 mmol）, $LiAlH_4$（1.5 mmol）, $Mn(OAc)_2$（0.025 mmol）, CH_3ONa（1.5 mmol）, THF（2 mL）, 20 h；b. Determined with an internal standard；c. 1 mmol $LiAlH_4$ was loaded；d. The isolated yields were respectively 71%（entry 2）, 62%（entry 8）, 73%（entry 15）；e. Beside of benzene（<2% yield）and phenol（<2% yield）, no other product was observed.

63% to 93% at 140 ℃（Entry 2 in Table 3 vs Entry 1 in Table 2），but the reductive cleavage of 4,4′-diphenyldiphenyl ether gave similar results as the base-free condition（Entry 3 in Table 3 vs Entry 2 in Table 2）. Different from the base-free method（Table 2, entry 8），both the aromatic C—O bonds of diphenyl ether moiety and the phenolic hydroxyl group of the resulting product were cleaved in the case of xanthene（Table 3, entries 4 and 5）. The addition of CH_3ONa was adverse for the reductive cleavage of benzofuran and decreased the yield from 92% to 75% in the case of 140 ℃（Entry 6 in Table 3 vs Entry 10 in Table 2）. The addition of CH_3ONa allowed diphenyl ether to be converted into the desired products in high yields（Table 3, entry 8），while the above-mentioned base-free method was less effective for this substrate（Table 2, entry 4）. 4, 4′-Dimethyldiphenyl ether also underwent this transformation smoothly, whereas its more sterically hindered o-constitutional isomer gave a lower yield（Table 3, entries 13 and 14），which suggested that the steric

hindrance had an important effect on the reaction. Similar with the results under the base-free condition, when benzyl phenyl ether and alkoxyl naphthalenes were used as the substrates, the alkyl C—O bonds were well cleaved over the aromatic C—O bonds, and only small amount of products from the cleavage of the aromatic C—O bonds were obtained.

To gain preliminary insights into the reaction mechanism, we performed several control experiments where TEMPO（2,2,6,6-tetramethylpiperidine 1-oxyl）was added as the radical scavenger into the reaction system shown in Scheme 1. As expected, the addition of 2 equiv. TEMPO led to no conversion of the dibenzofuran, which was consistent with the results reported in previous literatures[31]. These results suggest that the reductive cleavage of the aromatic carbon-oxygen bonds possibly proceed via radicals. Since the Mn compound can initiate radicals,[32−33] it seems to be reasonable that the Mn catalytic species plays a role of radical initiator.
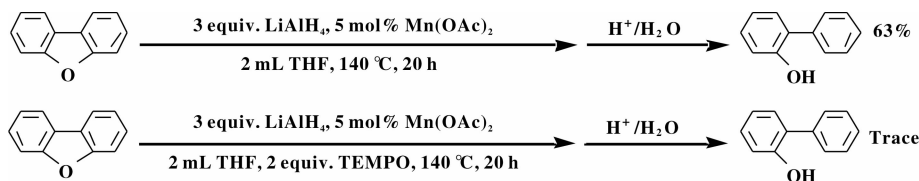
Scheme **1** Effect of TEMPO on the reductive cleavage of dibenzofuran

3 Conclusion

In conclusion, the Mn species was demonstrated to be a possible catalyst for the reductive cleavage of the aromatic carbon-oxygen bonds with $LiAlH_4$ as the reducing agent. The base-free method allowed a series of aromatic carbon-oxygen bonds to undergo the reductive cleavage with moderate to high selectivities under the catalysis of 5% $Mn(OAc)_2$. Although the reaction of diphenyl ethers gave the desired products in low yields, an addition of CH_3ONa could overcome this limitation. When the benzyl phenyl ether and alkoxyl naphthalenes were used as the substrates, the alkyl C—O bonds were well cleaved over the aromatic C—O bonds. Compared with the previous methods with Co or

Fe catalysts,[17,30] the base-free method with the Mn catalyst has the following advantages: the high base loadings is avoided in the case of some substrates, and the loading amount of the transition metal catalyst can be decreased from 20% or 15% to 5%. At the present stage, although our method is difficult to be applied into the practical processes such as selective organic synthesis and the lignin conversion due to the high $LiAlH_4$ loading and the narrow substrate scope, it is instructive to develop a novel way for the selective reductive cleavage of aromatic C—O bonds under the catalysis of the Mn compound.

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锰催化芳香碳-氧键的还原断裂

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摘要：这里发现锰化合物能够催化芳香碳-氧键的还原断裂. 就我们所知，目前还没有锰催化芳香碳-氧键断裂方面的报道. 以二苯并呋喃为底物，对各种反应条件进行优化，得到的较佳反应条件为 5% Mn（OAc）$_2$，3 当量 LiAlH$_4$，140 ℃温度，四氢呋喃溶剂. 在这个反应条件下，多种芳香碳-氧键能够发生还原断裂. 甲醇钠的添加能够有效地促进二苯醚等底物的反应. 对反应机理进行了初步研究，结果表明反应可能经历自由基过程.

关键词：还原断裂；碳-氧键；锰；催化