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MILD AND EFFICIENT NITRATION OF AROMATIC COMPOUNDS MEDIATED BY TRANSITION-METAL COMPLEXES

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GRAPHICAL ABSTRACT



Abstract Aromatic compounds were efficiently nitrated under facile reaction conditions by employing 69% nitric acid catalyzed by transition-metal complexes such as $[Co(NH_3)_5Cl]Cl_2$, $[Cu(NH_3)_4]SO_4$, $Mn(acac)_3$, $[Ni(NH_3)_6]Cl_2$, $[Ni(en)_3]S_2O_3$, and $Hg[Co(SCN)_4]$. The reaction was completed smoothly at room temperature and afforded corresponding mono-nitro derivatives in quantitative yield. This new method offers efficient and facile regioselective mononitration of aromatic compounds.

Keywords Aromatic nitration; nitric acid; regioselective; transition-metal complexes

INTRODUCTION

Nitration of organic compounds has long been a very active and rewarding area of research and is the subject of a large body of literature.^[1] Nitro aromatic compounds are extensively utilized as chemical feedstocks for the synthesis of a wide range of useful materials such as dyes, pharmaceuticals, perfumes, and plastics.^[2] The classical nitration procedure requires the use of a potent mixture of concentrated nitric and sulfuric acids, yielding large amounts of waste streams of inorganic acids, which are environmentally unfriendly and expensive to dispose of. In addition, the synthetic procedure is not very selective and often leads to overnitration or

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Scheme 1. Nitration of aromatic compounds mediated by transition-metal complexes.

by-products. The obvious disadvantages associated with these procedures prompted extensive research in finding new nitration methods such as the use of solid acid catalyst,^[3] different sources of NO₂,^[4] organic nitrating agents,^[5] metal nitrates,^[6] Lewis acids to replace sulfuric acid such as inorganic acidic salt (oxone),^[7] and rare-earth metals.^[8] With chemists under increasing pressure to perform atom-economical processes with minimal or no environmentally unfriendly by-products, development of a novel catalyst system that facilitate aromatic nitrations in this manner should be of great importance.^[9] In continuation of our work on environmentally friendly aromatic nitration using metal ions,^[10] we found that transition-metal complexes are efficient catalysts for the nitration of a wide range of aromatic compounds using stoichiometric quantities of nitric acid.

It is very well known that transition metals and their complexes efficiently accelerate a wide variety of organic reactions and have been successfully applied for catalytic epoxidation,^[11] oxidation,^[12] and hydrogenation.^[13] Although some transition-metal complexes recently have been used for the nitration of aromatics,^[14] surprisingly, the Werner type of transition-metal complexes^[15] has not been explored for aromatic nitration reactions so far. In continuation of our earlier work on nitration reactions,^[16] here we report the mild and efficient nitration of an aromatic compound mediated by transition-metal complexes (Scheme 1).

RESULTS AND DISCUSSION

A few Werner-type transition-metal complexes such as [Co(NH₃)₅Cl]Cl₂, [Cu(NH₃)₄]SO₄, Mn(acac)₃, [Ni(NH₃)₆]Cl₂, [Ni(en)₃]S₂O₃, and Hg[Co(SCN)₄] were chosen as the best candidates to promote the nitration of aromatics with nitric acid because it is easy to prepare these complexes.^[17] We have investigated the nitration of various aromatics by these complexes with nitric acid in dichloromethane at room temperature. To optimize the reaction condition, phenol was selected as a promising candidate for plausible nitration. The phenol (0.1 mol) and [Co(NH₃)5Cl]Cl₂ (0.1 mol) were taken in dichloromethane, and nitric acid was added to this mixture and stirred at room temperature. This layer chromatography (TLC) monitored the progress of the reaction. The products were isolated and analyzed by comparison with their characteristic spectroscopic data as reported in the literature. The nitration reactions performed with the other chosen transition-metal complexes revealed that all the Werner-type transition-metal complexes are quite effective in promoting the nitration of aromatics. Furthermore, the present nitration procedure was found to be applicable to a range of aromatics compounds as depicted in Tables 1 and 2. It is interesting to note that the present nitration work is under

	Substrate	Products ^{<i>a,b</i>}	Co(NH ₃) ₅ Cl]Cl ₂		[Cu(NH ₃) ₄ SO ₄		Mn(acac) ₃	
No.			Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)
1	Phenol	4-Nitrophenol	2	85	2.5	82	2.5	82
2	O-Cresol	4-Nitro-2-methylphenol	2	85	2.5	85	2.5	84
3	Acetanilide	2-Nitroacetanilide	2	85	2.5	85	2.5	85
4	Naphthalene	1-Nitronaphthalene	2	85	2	89	2	87
5	Toluene	4-Nitrotoluene	3	82	3	85	3	83
6	Chlorobenzene	4-Nitrochlorobenzene	2	82	2	85	2.5	80
7	Bromobenzene	4-Nitrobromobenzene	2	82	2	85	2.5	80
8	Salicylic acid	5-Nitrosalicylic acid	2.5	85	2.5	86	2.5	85
9	4-Methylacetanilide	4-Methyl-2-nitroacetanilide	2	82	2	84	2	83
10	Benzaldehyde	3-Nitrobenzaldehyde	2	82	3	84	2.5	85
11	Acetophenone	3-Nitroacetophenone	2	82	2	85	2	85
12	Benzophenone	3-Nitrobenzophenone	2	80	2.5	89	2.5	89
13	Benzoic acid	3-Nitrobenzoic acid	3	82	2.5	89	2.5	89
14	Benzonitrile	3-Nitrobenzonitrile	2.5	82	2.5	84	2.5	82
15	Benzamide	3-Nitrobenzamide	3	80	3	82	3	80

Table 1. Nitration of aromatic compounds mediated by transition-metal complexes

^aAll the products were characterized by the usual spectral and analytical methods. ^bIsolated yields.

heterogeneous conditions and therefore transition-metal complexes are easily separated from the reaction mixture by simple workup. Furthermore, it is also observed that nitration of aromatics proceeded rapidly and efficiently with the

	Substrate	Products ^{<i>a,b</i>}	[Ni(NH ₃) ₆]Cl ₂		Ni[(en) ₃]S ₂ O ₃		Hg[Co(SCN) ₄]	
No.			Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)
1	Phenol	4-Nitrophenol	2	80	2.5	82	5	72
2	O-Cresol	4-Nitro-2-methylphenol	2	82	2.5	80	5	74
3	Acetanilide	2-Nitroacetanilide	2	82	2.5	82	5	65
4	Naphthalene	1-Nitronaphthalene	2	80	2	80	5	77
5	Toluene	4-Nitrotoluene	3	82	3	83	5	73
6	Chlorobenzene	4-Nitrochlorobenzene	2	80	2	82	5	70
7	Bromobenzene	4-Nitrobromobenzene	2	80	2	82	5	70
8	Salicylic acid	5-Nitrosalicylic acid	2.5	80	2.5	82	5	75
9	4-Methylacetanilide	4-Methyl-2-nitroacetanilide	2	82	2	84	5	73
10	Benzaldehyde	3-Nitrobenzaldehyde	2	80	3	82	5	65
11	Acetophenone	3-Nitroacetophenone	2	82	2	82	5	75
12	Benzophenone	3-Nitrobenzophenone	2	82	2.5	80	5	69
13	Benzoic acid	3-Nitrobenzoic acid	3	80	2.5	80	5	69
14	Benzonitrile	3-Nitrobenzonitrile	2.5	80	2.5	80	5	72
15	Benzamide	3-Nitrobenzamide	3	82	3	82	5	70

Table 2. Nitration of aromatic compounds mediated by transition-metal complexes

^{*a*}All the products were characterized by the usual spectral and analytical methods. ^{*b*}Isolated yields.

present system without any overoxidation. In all the cases, nitration products we are obtained in quantitative yield within short times at room temperature. The reaction conditions are extremely mild as evidenced by the formation of 3-nitrobenzaldehyde from benzaldehyde without oxidation of aldehyde functionality. The reaction is carried out in various solvents such as ethyl acetate, ethanol, acetonitrile, and dichloromethane. Among all the solvents tried, the dichloromethane was found to be more suitable as it gives good yields of the product.

The structure of the nitrating complex and plausible mechanism are not clear at present. It is believed that the nitration is proceeding via the binding of nitric acid to the metal part of the transition-metal complex, which in turn releases a proton. The proton thus released further reacts with another molecule of nitric acid and liberates the nitronium ion (NO₂⁺). Nitro aromatics are produced when this NO₂⁺ ion attacks the aromatic ring. Further work to explore this mechanism of the reaction is in progress.

CONCLUSION

In summary, the use of the transition-metal complex–nitric acid system is simple, fast, and mild for the nitration of aromatic ring. The reaction is tolerant to a range of functional groups and gives quantitative yields. Thus, this new method offers efficient and facile regioselective mononitration of aromatic compounds.

EXPERIMENTAL

The general procedure is as follows: To a solution of phenol (1 mmol) in dichloromethane, 69% of nitric acid (1 mmol) and 1 mmol of transition-metal complex ([Co(NH₃)₅Cl]Cl₂) were added, and the reaction mixture was stirred at room temperature for 2 h. The progress of the reaction was monitored by TLC. After the completion of reaction as indicated by TLC, the reaction mixture was treated with sodium carbonate solution. The reaction mixture was extracted with dichloromethane. The organic layer was separated, dried over sodium sulfate, and evaporated to give the crude product. The crude product was purified over silica gel to get 4-nitrophenol as the product in 85% yield.

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