

Nitrations Using Metal Nitrates - Trifluoroacetic Acid Systems

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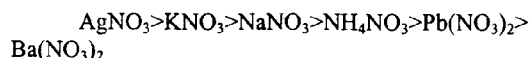
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Summary: nitrations of halobenzenes with metal nitrates in trifluoroacetic acid at 90°C have been carried out successfully.

Introduction

Nitration is one of the most basic and important reaction in organic chemistry and is used for the preparation of nitro compounds. Both aliphatic and aromatic compounds can be nitrated, however the reaction has more significance in aromatic chemistry [1-3]. A wide variety of nitrating agents have been reported in literature [1-3], however, the use of metal nitrates has received much attention due to their mildness, easy handling, easy to control the extent of nitration and better selectivity.

Nitration of phenol with copper nitrate in acetic anhydride has been reported by Menke in old literature [4]. Cornélis *et al.* [5] have studied the nitration of toluene by using a series of metal nitrates in different solvents including acetic anhydride at various temperatures. Gigante *et al.* [6] have reported the nitration of aromatic compound with cupric nitrate impregnated on montmorillonite (claycop) in acetic anhydride. Laszlo and Pennetreau [7] have claimed that halobenzenes can be mono nitrated with claycop in hexane or in dichloromethane containing acetic anhydride with *para* preference. Cornélis *et al.* [8] have stated that K10 clay – supported ferric nitrate (clayfen) is an efficient nitrating agent of phenol leading to mono nitration under extremely mild reaction conditions with a nice regioselectivity. Samajdar *et al.* [9] have reported that bismuth nitrate in the presence of montmorillonite in tetrahydrofuran can be used for mono nitration of reactive aromatic substrates. Dove *et al.* [10] have claimed that vanadium (V) oxytrinitrate in dichloromethane is a powerful and easy to handle nitrating agent. A series of substituted aromatic rings have been nitrated with this reagent with very high yield. Topchiev *et al.*, [11] have tried various inorganic nitrates in the presence of various Lewis acids under heterogeneous conditions. The order of the reactivity under these conditions was found to be:



Olah *et al.*, [12] have demonstrated the nitration of benzene, ethylbenzene and bromobenzene with silver nitrate-boron trifluoride in ethanenitrile. An efficient method for mono- and dinitration of aromatic substrates have been developed by Chawla and Mittal [13]. They used ceric ammonium nitrate without solvent on silica gel for mononitration and with solvent for dinitration. Mellor *et al.* [14] have also reported the nitrations of aromatic substrates by using ceric ammonium nitrate suspended in dichloromethane in the presence of two equivalent of sulfuric acid. Kwok *et al.* [15] have described the mononitration of toluene with high *para* regioselectivity with praseodymium nitrate in the presence of H-ZSM-5 zeolite (Si/Al ratio = 1000). Quartani *et al.* [16] have reported that mononitration of phenols can be achieved at room temperature with sodium nitrate in a two phase system (water-ether), in the presence of hydrochloric acid and a catalytic amount of lanthanum nitrate. Sastry and Kudav [17] and, Iqbal and Aslam [18] have employed a mixture of potassium nitrate and polyphosphoric acid for the mononitration of deactivated aromatic rings. Umeura *et al.* [19] have reported that sodium nitrite or sodium nitrate in trifluoroacetic acid can be used for the nitration of alkylbenzenes at 25°C. Makhon'kov *et al.* [20] have reported the nitration of benzene with ammonium nitrate in trifluoroacetic acid at 20°C.

Results and Discussion

In the present work we wish to report the nitrations of halobenzenes with various metal nitrates in trifluoroacetic acid. Thus sodium nitrate, potassium nitrate, ammonium nitrate and cadmium nitrate in trifluoroacetic acid at 90°C were used for the

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Table-1 (Nitro Derivatives of Halobenzenes)

Serial No.	Reactant	Metal nitrate	Product	Yield (%)	Mp.(°C)
1	Chlorobenzene	sodium nitrate	4-nitrochlorobenzene	45	80-82 (83)
2	Chlorobenzene	potassium nitrate	4-nitrochlorobenzene	51	82-83 (83)
3	Chlorobenzene	ammonium nitrate	4-nitrochlorobenzene	54	81-82 (83)
4	Chlorobenzene	cadmium nitrate	4-nitrochlorobenzene	50	82-83 (83)
5	Bromobenzene	sodium nitrate	4-nitrobromobenzene	74	126-127 (127)
6	Bromobenzene	potassium nitrate	4-nitrobromobenzene	70	125-126 (127)
7	Bromobenzene	ammonium nitrate	4-nitrobromobenzene	79	126-127 (127)
8	Bromobenzene	cadmium nitrate	4-nitrobromobenzene	74	124-127 (127)
9	Iodobenzene	sodium nitrate	4-nitroiodobenzene	76	172-174 (174)
10	Iodobenzene	potassium nitrate	4-nitroiodobenzene	80	173-174 (174)
11	Iodobenzene	ammonium nitrate	4-nitroiodobenzene	81	173-174 (174)
12	Iodobenzene	cadmium nitrate	4-nitroiodobenzene	74	172-174 (174)

Melting points given in parenthesis are the literature melting points [21]

nitration of chlorobenzene, bromobenzene and iodobenzene. Only the *para*-nitrohalobenzenes were isolated. The yields are satisfactory to excellent (table-I). A change of the counter-cations of nitrate [NaNO_3 , KNO_3 , NH_4NO_3 , $\text{Cd}(\text{NO}_3)_2$] makes little effect on the results of nitration. The products were identified by comparing their observed melting points to those reported in literature (table-I). In conclusion, a mild and efficient general procedure for mononitration of mildly deactivated aromatics has been developed which because of its experimental simplicity, its selectivity, and its ability to be applied to deactivated substrates, should find wide application.

Experimental

Melting points (uncorrected) were determined on Gallenkamp melting point apparatus. All the chemical used were purchased from Fluka.

General Procedure

A mixture of halobenzene (10 mmol) and inorganic nitrate (10 mmol) in trifluoroacetic acid (10 mL) was heated under reflux with stirring for two hours at 90°C. The reaction contents were poured in ice-cold water (50 mL). On pouring, fine crystals of aromatic nitro compounds were formed. These crystals were filtered and dried. The crude product was recrystallized from ethanol.

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