

The Phthaloyl chloride-Induced Conversion Reactions of Trinitrobenzene into Nitroaryl Halides

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The demilitarization of TNT, DNT and ammonium picrate in Russia and the West is producing million pounds of surplus energetic materials. These have been disposed by open burning/detonation. The use of open burning/detonation is becoming unacceptable due to public concern and environmental regulations. Therefore, the chemical conversion study of surplus energetic materials to higher value products would be highly desirable.¹ The West have used TNT as a versatile starting material for the design of different types of valuable products.²

During our research on conversion of TNT and DNT into high valuable raw materials in fine chemical industry, we reported synthesis of Phloroglucinol from TNT.³ Herein we describe a synthesis of nitroaryl halides from TNB by substitution of nitro group with halogen atom.

The introduction of halogen atoms into aromatic compounds is one of the difficult operations in organic chemistry. The conventional methods proceeded by the Sandmeyer reaction⁴ are unsatisfactory from the point of view of industrial application. Another substitution method promoted by potassium fluoride from nitroaryl compound showed the unsatisfactory result (Figure 1).⁵

On the other hand, the acid halide-aided substitution reactions of nitroaryl compounds with KF have been received great attention in the field of fluorine chemistry due to relatively easy introduction of fluorine atom. However, only KF have been utilized for this transformation and this conversion method is still required to improve the yield of product.⁶

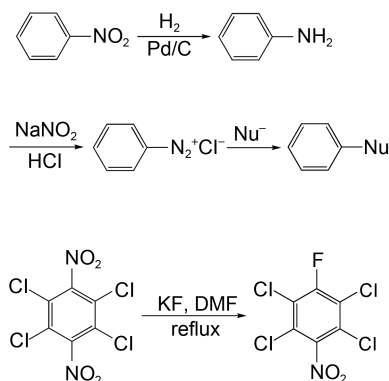


Figure 1. The synthetic schemes of aryl halides from nitroaryl compounds.

We examined the reactions of TNB prepared from TNT with LiF, NaF, KF and CsF in the presence of phthaloyl chloride and sulfolane. As expected,⁶ the use of CsF gave good yield of the 1-fluoro-3,5-dinitrobenzene (**1**) and 1,3-difluoro-5-nitrobenzene (**2**), while the use of KF, NaF and LiF gave poor yield or no products (Table 1, Figure 2). In case of X⁻ (X: halogens) in the protic solvents, nucleophilicity increases going down the periodic table; for example, nucleophilicity decreases in the order I⁻ > Br⁻ > Cl⁻ > F⁻. However, in case of X⁻ in the aprotic solvents such as DMSO, DMF and sulfolane, nucleophilicity decreases in the order F⁻ > Cl⁻ > Br⁻ > I⁻. Because the cations associated with nucleophilic anions are strongly solvated in aprotic solvents, the anions are dissociated from the cations, which further enhance their nucleophilicity. In the presence of protic solvent, presumed intermediate was decomposed by protic solvent (Figure 3). Therefore, we got fluorobenzene compounds easier than other aromatic halogen compounds.

To evaluate the scope of this system, the range of metal salts was extended to various metal halides. Among the different metal halides, chlorides and bromides were found to afford a only 1-chloro-3,5-dinitrobenzene (**3**) and 1-bromo-3,5-dinitrobenzene (**4**) respectively with poor yield (Table 1, Figure 2). It was also observed that reaction of iodine metal salts did not give any product.

Therefore, the aryl fluoride is more easily prepared than other aryl halides. In the presence of protic solvent, the

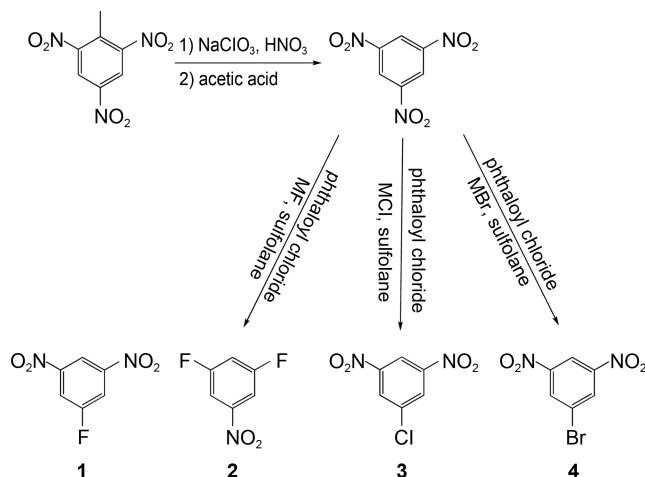


Figure 2. The synthetic scheme of nitroaryl halides from TNT.

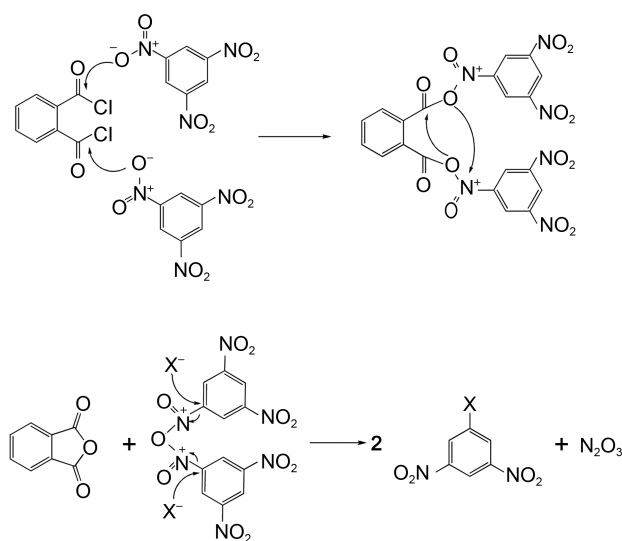


Figure 3. The proposed formation mechanism for nitroaryl halide.

reaction did not work at all since phthaloyl chloride was attacked by the solvent (Figure 3).

To optimize the reaction condition, the minimum requirement of both phthaloyl chloride and metal halides relative to TNB was investigated in sulfolane. Such systematic study did not show any significant difference of the result (Table 1). The reaction was also carried out in various organic solvents such as DMSO, DMF, NMP, and CH₃CN and did not improve the yield of the product. A possible reaction mechanism for this aromatic substitution reaction is proposed in Figure 3.

Table 1. The reactions of 1,3,5-trinitrobenzene (TNB) with halide ions

MX	Equiv.	Product	Time (h)	Temp (°C)	Yield (%) ^a
LiF NaF	6	-	16	210	- ^b
KF	4	1	12	180	35
	6	2	12	200	40
CsF	4	1	8	140	85
	6	2	8	180	87
LiCl			10	200	10
NaCl			10	200	14
KCl	5	3	9	180	20
CsCl			9	180	17
LiBr			11	200	10
NaBr			11	200	10
KBr	5	4	12	210	8
CsBr			12	210	7
LiI					
NaI	6	-	16	210	- ^b
KI					
CsI					

^aIsolated yield. ^bNone of the desired products.

In summary, we have prepared some nitroaryl halides from TNB in the presence of acid halide and X⁻. Main advantage of this work is that reaction of nucleophilic aromatic substitution with X⁻ proceeded. The future work including other nucleophile except halide ions is under investigation in our laboratory.

Experimental Section

General. All proton nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity Inova spectrometer at 300 MHz and are reported in parts per million (ppm) on the δ scale relative to chloroform-*d*₁. Analytical thin layer chromatography (TLC) was performed with E. Merck pre-coated TLC plates, silica gel 60F-254, layer thickness 0.25 mm. Column chromatography was done with silica gel 60 (70-230 mesh ASTM) from E. Merck mostly by gravity.

1-Fluoro-3,5-dinitrobenzene (1)⁶: 1,3,5-Trinitro benzene (1.0 g, 4.69 mmol), CsF (2.85 g, 18.78 mmol) and phthaloyl chloride (0.95 g, 4.69 mmol) together in sulfolane (10 mL) are heated to 140 °C for 8 h. The reaction mixture was allowed to cool to room temperature, and it was extracted with diethyl ether (15 mL) and 3 M NaOH solution (3 × 10 mL), washed with water (10 mL). The combined organic layers were dried over anhydrous MgSO₄ and solvent was removed under reduced pressure to obtain the crude product. Pure product was obtained by chromatography as yellow solid. mp 43-44 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.91 (q, *J* = 1.8 Hz, 1H), 8.32 (dd, *J* = 7.5, 1.8 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 162.2 (d, *J* = 257 Hz), 149.3 (d, *J* = 7.5 Hz), 117.3 (d, *J* = 26.7 Hz), 115.0 (d, *J* = 3.5 Hz).

1,3-Difluoro-5-nitrobenzene (2)⁶: mp 17 °C; bp 176-177 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.79 (m, 2H), 7.21 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 162.7 (dd, *J* = 190.1, 9.1 Hz), 149.7 (t, *J* = 8.3 Hz), 110.4 (t, *J* = 18.9 Hz), 107.8 (dd, *J* = 16.2, 6.0 Hz).

1-Chloro-3,5-dinitrobenzene (3)⁷: mp 54-55 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.97 (t, *J* = 1.8 Hz, 1H), 8.58 (d, *J* = 1.8 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 149.0, 137.2, 129.5, 117.5.

1-Bromo-3,5-dinitrobenzene (4)⁸: mp 74-76 °C; ¹H NMR (300 MHz, CDCl₃) δ 9.03 (t, *J* = 1.8 Hz, 1H), 8.74 (d, *J* = 1.8 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 148.8, 132.1, 123.9, 117.8.

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