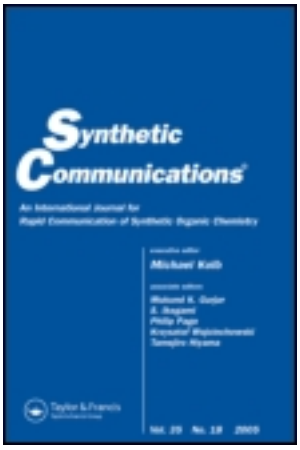

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A Convenient Method for the Oxidation of Aromatic Amines to Nitro Compounds Using Tetra-n-alkylammonium Bromates

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A Convenient Method for the Oxidation of Aromatic Amines to Nitro Compounds Using Tetra-*n*-alkylammonium Bromates

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ABSTRACT

Tetra-*n*-propyl and tetra-*n*-butylammonium bromates were used for the oxidation of a variety of aromatic amines to nitro compounds. Reaction condition and recovery simple and yield of products high.

Key Words: Aromatic amines; Nitro compounds; Quaternary ammonium salts; Oxidants.

INTRODUCTION

Quaternary ammonium salts, as phase transfer catalysts have been used to catalyze oxidation of a variety of substrates using oxidants such as O_2,[1]

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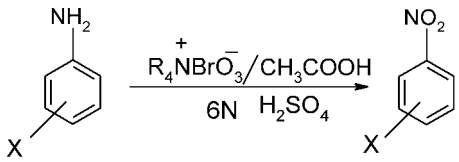
NaOCl,[2] H_2O_2,[3] $KMnO_4$, and others.[4,5] In our search for low cost, sensitive, and easy to handle oxidizing agents, we found that the tetra-*n*-alkylammonium bromates prepared from the corresponding tetra-*n*-alkylammonium bromides by using chlorine gas in an alkaline medium are useful for the oxidation of organic substrates. Direct oxidation of aromatic amines to nitro compounds were reported by using many reagents.[6–11] However, these methods of oxidation had limitations due to formation of side products formed mainly from the partial oxidation of the amines, giving moderate yields. In the present study, the versatility of the tetra-*n*-propylammonium bromates and tetra-*n*-butylammonium bromates as oxidizing agents is established by the fact that several aromatic amines could be oxidized to the nitro compounds using simple reaction techniques. Further, work up was simple and the products were obtained in high yields (Sch. 1; Table 1).

EXPERIMENTAL

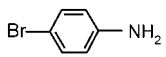
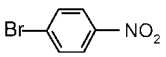
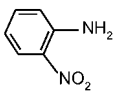
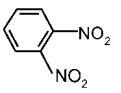
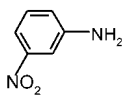
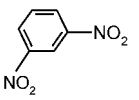
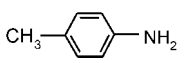
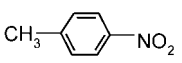
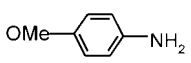
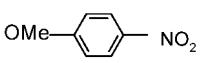
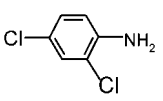
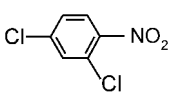
General Procedure for Conversion of Tetra-*n*-alkylammonium Bromides to Bromates

10 mmol of tetra-*n*-alkylammonium bromide was dissolved in 50 mL of 5% aqueous NaOH and chlorine gas was passed through the solution till a yellow oil separated, which solidified on standing. The yellow solid was filtered and dried. Neutralizing the filtrate with acetic acid, precipitated more products. Using this procedure, both the tetra-*n*-propyl ammonium bromate and tetra-*n*-butylammonium bromate were prepared. Tetra-*n*-propylammonium bromate (m.p. 114°C, yield 74%) Found: C, 46.2%; H, 9.15%; N, 4.18%; requires C, 45.86%; H, 8.92%; N, 4.46%. ^{1}H-NMR δ ($CDCl_3$) 1.2 (3H, t) 2.3 (m, 2H), 4.5 (t, 2H) and tetra-*n*-butylammonium bromate (m.p. 61–63°C, yield 70–75%). Found: C, 50.86%; H, 9.92%; N, 3.93%; requires C, 51.88%; H, 9.73%; N; 3.78%. ^{1}H-NMR, δ ($CDCl_3$) 1.3 (3H, t), 2.3 (m, 2H), 4.8 (t, 2H).



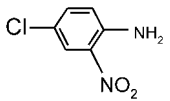
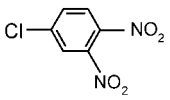
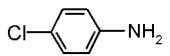
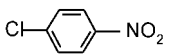
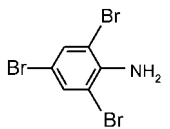
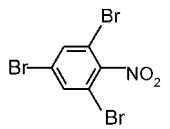
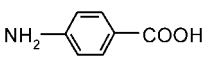
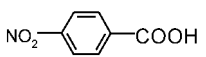
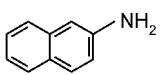
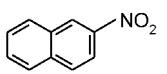
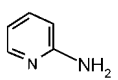
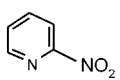
Scheme 1. Oxidation of aromatic amines to nitro compounds.

Table 1. Oxidation of various aromatic amines to nitro compounds.

S. no	Aromatic amine	Nitro compound[a]	Reflux time (min)		Yield (%)		M.p. (°C)	
			I	II	I	II	Observed	Literature
1			60	110	84	70	125–126	127
2			75	110	88	75	120	118
3			90	125	92	60	90	90
4			80	95	90	84	54	52
5			90	145	88	70	56	53
6			90	105	81	75	63	66

(*continued*)

Table 1. Continued.

S. no	Aromatic amine	Nitro compound[a]	Reflux time (min) I	Reflux time (min) II	Yield (%) I	Yield (%) II	M.p. (°C) Observed	M.p. (°C) Literature
7			90	110	86	45	105	—
8			75	90	84	82	85	83
9			60	95	79	65	97	—
10			90	80	74	55	246	241
11			90	125	78	70	73–74	79
12			600	720	40	55	82	75

Note: I indicates oxidation with tetra-*n*-propylammonium bromate and II with tetra-*n*-butylammonium bromate.
[a]Products were characterized by IR, ^{1}H-NMR, and mass spectra and by comparing the observed m.p. to those found in literature.
[b]For 2-aminopyridine, a slow stream of air was passed through the reaction solution during reflux reaction carried out in ethanol solution without sulfuric acid and acetic acid.

General Procedure for the Oxidation

1 mmol of aromatic amine was dissolved in 20 mL of glacial acetic acid followed by addition of 2 mmol of the tetra-*n*-alkylammonium bromate and 5 mL of 6 N H_2SO_4. The solution was refluxed and monitored by TLC. The reaction was brought to room temperature and poured on crushed ice and solid filtered. Solid was purified by dissolving in ethanol and poured over water. The same reaction was also performed by using tetra-*n*-butylammonium bromate and similar results were obtained. The products were identified by comparing melting points of the products with those found in literature [12] and by comparision of ^{1}H-NMR spectra. In conclusion, we have devised a simple method for the preparation of tetra-*n*-alkylammonium bromates and used them for the oxidation of aromatic amines to nitro compounds in high yields.

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