

AN ELEGANT AND COST -EFFECTIVE METHOD OF AROMATIC BROMINATION USING SODIUM BROMIDE AND HOUSEHOLD BLEACH

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ABSTRACT

Sodium bromide in presence of 1(M) HCl with common household bleach generates bromine in situ and undergoes aromatic electrophilic substitution reaction selectively in good yield in a mild reaction condition. This is a very cost effective, elegant, water based method for activated aromatic bromination reported for the first time.

Keywords: cost-effective, household bleach, bromination, aromatic bromination,

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INTRODUCTION

Aromatic electrophilic bromination reaction is a fundamental and useful reaction in organic chemistry. The aromatic bromo compounds can be used as potent antitumor, antibacterial, antifungal, antineoplastic, antiviral and anti oxidizing agent¹. Moreover the aromatic bromo compounds are important precursor of Grignard reagents². The weak C-Br bond facilitates the oxidative addition of aryl bromides to low valent transition metals, resulting in Ar-M-Br intermediate, which provides new synthesis of arene carboxylic acids, esters and alcohols.

For the vast usefulness of aromatic bromo compounds several traditional, non traditional methods for aromatic bromination are adopted in far flung laboratories around the world for many years. Among traditional methods hazardous liquid bromine was used³. Many researchers used costly pyridiniumtribromide as a bromine source⁴. The other methods include palladium catalyzed bromination, ammonium bromide/hydrogen peroxide, LiBr/ Ceric ammonium nitrate, KBr/Oxone , KBr/ KBrO₃, HBr/t-butyl hydro peroxide⁵⁻⁹. The replacement of these expensive oxidants by non toxic cheaper common household bleach (NaOCl, 4% W/V) is a challenge in the bromination of activated aromatic compounds. Herein we report an elegant, environmentally safe procedure of bromination with NaBr as a bromine source in very mild acidic condition with 4% NaOCl solution which involves simple work up.

EXPERIMENTAL

The test reaction was carried out on acetanilide in aqueous alcohol with NaBr and NaOCl in the presence of 1(M) HCl acid at 0°C for 2hr. to give p-bromo acetanilide.

General procedure for bromination of aromatic compounds

To acetanilide (1g, 7.4mmol) in aqueous alcohol was added NaBr (0.823g, 8mmol) and 7ml 1(M) HCl in a r.b. flask. The mixture was stirred rapidly. Then NaOCl 5ml (4%w/v) was added drop wise through a pressure equalizer for an about 75 minutes. After each addition, a yellow precipitate appeared soon disappeared. After complete addition of NaOCl, an off white precipitate appeared, filtered and washed with dilute sodium bisulphite solution and then with water, crystallized from 95% ethanol. (1.56g, 98%) m.p.163 °c (lit 163 °c). In some cases after completion of the reaction (measured by TLC monitoring), the reaction mixture was extracted with diethyl ether (40ml) .

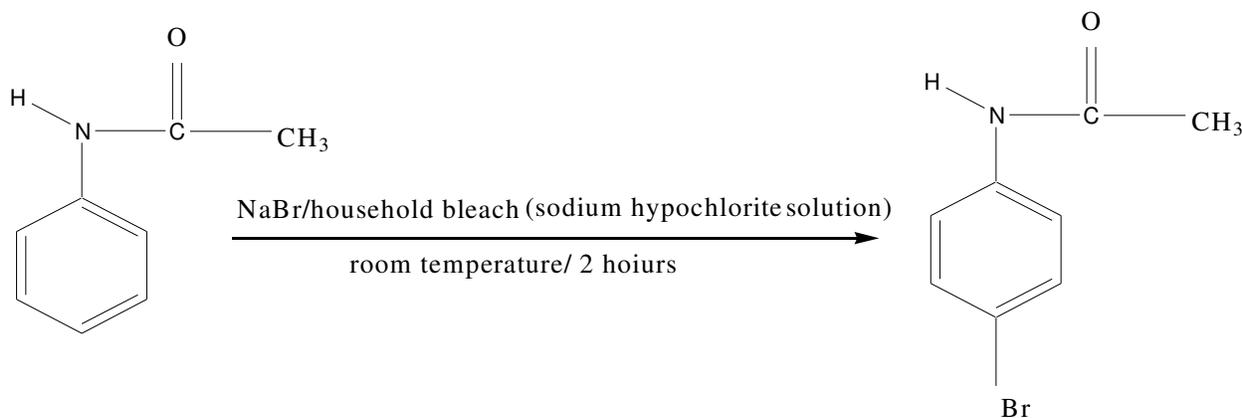
The ether extract was washed with 5% aqueous sodium thiosulphate and water and dried over anhydrous Na₂SO₄. Removal of the solvent gave a residue which was purified on silica gel using hexane as eluent to afford the desired bromo compound.

¹HNMR spectral analysis and ¹³CNMR spectra were measured with a Varian Gemini 400-MHz spectrophotometer.

p-Bromo acetanilide

¹HNMR (d₆ DMSO) δ 2.04(s, 3 H,methyl), 7.45 (d,J= 8.34Hz,2H) 7.56(d,J= 8.52Hz,2H),10.06(broad s,1H,NH) ppm.

¹³C NMR (d₆ DMSO) δ 24.4(CH₃), 114.9(CH), 121.3(CH), 131.9(C-1), 139.1(C-4), 168.9 (carbonyl carbon).



Scheme-1
Table-1

| Entry | Substrate | Temp.(°c)/ Time(h) | Product | M.P.(°c) | Yield% ^d |
|-------|------------------------|-----------------------|---|------------|---------------------|
| 1 | Acetanilide | rt/2 | 4--bromoacetanilide | 169-170 | 98 |
| 2 | vanillin | 0-5 /2 | 5-bromo- vanillin | 164-166 | 80 |
| 3 | 2-naphthol | 5-10/ 2 | 1-bromo-2-naphthol | 84-85 | 75 |
| 4 | Salicylic acid | 40-50/3 | 5-bromo-salicylic acid | 203-205 | 85 |
| 5 | p-hydroxy benzoicacid | 0-5 /2 | 3-bromo-p-hydroxybenzoic acid | 176-178 | 90 |
| 6 | p-methoxy benzoic acid | rt/overnight | 3-bromo-p-methoxybenzoic acid | 220-222 | 95 |
| 7 | phenol | 5-10/2 | bromo phenol ^a | 61-62 | 94 |
| 8 | p-cresol | 0-5/2 | 2,bromo-4-methyl phenol | 213-214 °c | 74 |
| 9 | aniline | 0/2 | bromo aniline ^b | 56-58 | 75 |
| 10. | Cinnamic acid | 50/2 | Erythro-2,3-dibromo-3-phenyl-propanoic acid | 203-205 | 75 |

^aPara: ortho ratio 94:6 by GC analysis

^bPara: ortho ratio 80:20 by GC analysis

^cboiling point

^dAll the compounds showed satisfactory spectroscopic data

RESULTS AND DISCUSSION

A number of different activated aromatic compounds with both electron withdrawing and electron donating groups are subjected to the bromination reaction to prove the generality of this method and the

results are summarized in Table I. As expected all the substrates underwent bromination reaction in excellent yield of mono brominated product.

The Table-1 summarizes the results on electrophilic aromatic bromination with household bleach and sodium bromide.

CONCLUSION

In conclusion we can say that there are only a handful of methods for water based aromatic bromination. The method described here develops a cost effective, elegant and safe procedure for bromination of aromatic compounds. In future the direct handling of bromine should be avoided in chemical laboratories to give a clean and safe environment

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