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A CONVENIENT METHOD FOR BROMINATION OF AROMATIC AMINES

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ABSTRACT: Pyridinium hydrobromide perbromide has been used to monobrominate aromatic amines. The monobromo compounds are obtained in good yield and with only small amounts of polybromoination products.

Pyridinium hydrobromide perbromide ($PyHBr_3$) has been used for the bromination of ketones[1], for the addition of bromine to alkenes[2,3], for dehydrohalogenation[4], and for the selective bromination of dienes[5]. However, as a reagent for bromination of aromatic systems, $PyHBr_3$ has been limited to bromination of pyridine under severe conditions[6], and the conversion of indole into 3-bromoindole[7]. The kinetics of bromination of various aromatics also has been studied.[8]

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TABLE

PRODUCT DISTRIBUTION

Starting Amine	%Mono sub.	(o/p)	%Disub.
Aniline*	87	(19/68)	5
Aniline	-	----	98
N,N-Dimethylaniline	95	(1/94)	<1
o-Anisidine	82	(17/65)	7
p-Anisidine	77	----	16
m-Anisidine	76	(14/28)	47
o-Toluidine	79	(15/64)	13
p-Toluidine	81	----	11
m-Toluidine	76	(14/28)	11
N-Methylaniline	86	(8/78)	2
N-Ethylaniline	91	(6/85)	-
o-Ethylaniline*	91	(12/79)	-
p-Nitroaniline*	76	----	-
Ethyl-p-aminobenzoate	75	----	-
2-Methoxy-5-methylaniline *	91	----	-
Ethyl-p-dimethylaminobenzoate*	86	----	-
2-Aminopyridine	92	----	-

* Treated with 5 mL of 10% HCl.

We wish to report that $PyHBr_3$ is a convenient reagent for the selective monobromination of activated aromatic amines. Aniline or an activated aromatic amine, dissolved in tetrahydrofuran, is treated dropwise with $PyHBr_3$ in THF with stirring at room temperature. In most cases the monobromo derivative is formed in good yield (see table) and with only minor amounts of di-or tribromo-substitution products. Generally mixtures of ortho and para products were obtained with the para isomer predominating.

The bromination appears to be very sensitive to the presence of electron withdrawing groups. Both the p-nitroaniline and the ethyl-p-dimethylaminobenzoate required added acid to produce an appreciable yield of brominated product. When aniline was brominated in the presence of acid, the reaction yielded exclusively the dibromo product.

It is also obvious from the very low amount of ortho product in the case of N-substituted amines that steric requirements are important. In all cases the product formed seems to be under the directive control of the amino group.

The unusually large amount of dibromo product produced upon bromination of m-anisidine may be attributed to the two doubly activeated positions.

Experimental

Pyridinium hydrobromide perbromide[9] (0.001 mole) was dissolved in THF (25 mL). An aromatic amine (0.001 mole) and an internal standard, decane (0.001 mole), were dissolved in a separate 25 mL portion of THF. The pyridinium hydrobromide perbromide solution was added dropwise over a 45 minute period to the amine solution which was stirred magnetically. After completing the addition, the solution was stirred for an additional 15 minutes. The solution was filtered

to remove any salt (probably pyridinium hydrobromide) which had separated. The filtrate was treated with sodium bisulfite to remove any excess bromine, filtered, dried ($MgSO_4$) and analyzed by GC-MS (Hewlett-Packard 5890 GC with HP Ultra 1 [Crosslinked Methyl Silicone Gum] 12m x 0.2mm column; HP 5971A MS).

Several of the reactions (* in Table) were conducted exactly as described above except the amine/THF solution was treated with 5 mL of 10% HCl prior to addition of the $PyHBr_3$.

Isolation of p-Bromoaniline:

Aniline (0.001 mole) was brominated in THF as described above. The progress of the reaction was monitored by GC-MS. Upon disappearance of the aniline the reaction was treated with sodium bisulfite, washed and dried as previously described. The solvent was removed and the residue subjected to bulb to bulb (0.35 Torr) distillation after being degassed several times. The p-bromoaniline (145 mg, 84%) obtained was identical with an authentic sample by GC-MS and FTIR.

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