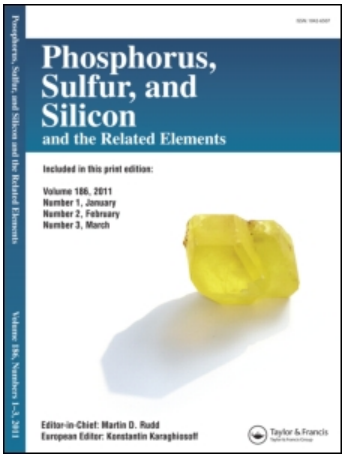

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Adel Amer[a]; Andrea Mayer[a]; Gary M. Conroy[a]; Hans Zimmer[a]
[a] Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, USA

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N-SUBSTITUTED AMINOTRIPHENYLPHOSPHONIUM TRIBROMIDES AS NOVEL BROMINATING AGENTS

ADEL AMER,[1] ANDREA MAYER, GARY M. CONROY and HANS ZIMMER*
Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221-0172, USA

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A number of N-substituted aminotriphenylphosphonium tribromides were investigated for their brominating ability of substituted phenols. It was found that *t*-butylaminotriphenylphosphonium tribromide, **I**, exhibits a good and a rather high regiospecificity in comparison with the commonly used bromine.

Key words: N-alkylaminotriphenylphosphonium tribromides, *t*-butylaminotriphenylphosphonium tribromide, bromination, phenols.

INTRODUCTION

The utility of a number of N-substituted aminotriphenylphosphonium tribromides as novel brominating agents for phenols was investigated. It was found that N-*t*-butylaminotriphenylphosphonium tribromide **I** acts as a mild, and more important, a selective brominating agent for a number of substituted phenols. Though several ammonium trihalides[2–8] have been known to also brominate certain aromatics, **I** not only for its selectivity but for its long shelf life seems to be a more desirable brominating agent than the known ammonium trihalides.

RESULTS AND DISCUSSION

Several substituted phenols were reacted with a calculated amount of *t*-butylaminotriphenylphosphonium tribromide, **I**, in dichloromethane-methanol at room temperature. Methanol was added to increase the activity of the tribromide for the electrophilic aromatic substitution. The results obtained by GC mass spectroscopic analysis are listed in Table I. For comparison the reactions were also performed with bromine instead of the tribromide under identical reaction conditions and molar ratios. The results for the comparative brominations with bromine are shown in Table II.

The results indicate that **I** is a more selective brominating agent for substituted phenols. Generally, monobrominated products are formed, whereas bromine usually gives a mixture of mono- and dibrominated phenols.

Moreover, the novel brominating agent shows a high degree of regiospecificity, while bromine often leads to isomeric bromination products. The reaction of 3,5-dichlorophenol with an equimolar amount of the **I** gave a mixture of dibromo- and monobromo-substituted phenols, with one of the two dibromo-substituted phenols being the predominant product. By the bromination of 3,5-dichlorophenol with bromine, however, no preferred dibromo-substituted phenol is found. Also, the reaction

TABLE I

Bromination of phenols with *t*-butylaminotriphenylphosphonium tribromide

Substrate	Molar Ratio Br_3^-/ Substrate	Products (% integrated peak area) [a] Substrate	Monobromo-derivatives	Dibromo-derivatives	Other [d]
4-tert-butyl-phenol [b]	1	4.88	94.27	-	0.85
3-tert-butyl-phenol [b]	1	0.98	98.51	-	0.50
3,5-dimethyl-phenol [b]	1	1.02	95.28	-	3.70
3,5-di-tert-butylphenol [b]	1	1.36	98.64	-	-
3,5-di-tert-butylphenol	3	-	77.93	20.70 [e]	1.37
3,5-dichloro-phenol [b]	1	-	64.78	1.59 and 31.59 two peaks	2.04
2-nitro-phenol [c]	1	62.83	20.69 and 3.14 two peaks	5.43	5.43
2-nitro-phenol	2	3.27	20.04 one peak	76.69	-

a) Products were investigated by GC mass spectroscopy of the reaction mixtures and calculation of the percentage of the peak areas.
b) Average value obtained from two performed reactions.
c) Average value obtained from three performed reactions.
d) Traces of unidentified reaction products/impurities.
e) The structure(s) of the dibrominated product(s) in all reported runs was (were) not determined.

of 2-nitrophenol with the phosphonium tribromide favored the formation of only one of the monobromo-substituted phenols suggesting that the steric bulk of the cation of the novel brominating agent **I** is responsible for the observed regiospecificity.

For comparison different N-substituted aminotriphenylphosphonium tribromides including the unsubstituted amino species were also investigated for their brominating ability. These compounds, however, showed no advantage over the brominating reactions obtained with **I**. These results are reported in Table III. Moreover, **I** has a much longer shelf life than the tribromides listed in Table III.

Further results involving other halogenation reactions with different N-alkylaminotriphenyl trihalides will be reported shortly.

TABLE II

Bromination of phenols with elemental bromine

Substrate	Molar Ratio Br_3^-/ Substrate	Products (% integrated peak area) [a] Substrate	Monobromo-derivatives	Dibromo-derivatives	Other [d]
4-tert-butyl-phenol [b]	1	1.05	79.74	19.21	-
3-tert-butyl-phenol [b]	1	traces	87.59	11.74	0.67
3,5-dimethyl-phenol [c]	1	25.24	32.34	42.42	tribromo-derivative, traces
3,5-di-tert-butylphenol [b]	1	-	100.00	-	-
3,5-di-tert-butylphenol	3	-	-	100.00	-
3,5-dichloro-phenol [c]	1	-	51.61	28.49 and 19.45 two peaks	0.45
2-nitro-phenol [b]	1	24.81	35.42 and 11.83 two peaks	26.78	1.16
2-nitro-phenol	2	10.08	61.36 and 9.41 two peaks	19.15	-

a) Products were investigated by GC mass spectroscopy of the reaction mixtures and calculation of the percentage of the peak areas.
b) Average value obtained from two performed reactions.
c) Average value obtained from three performed reactions.
d) Traces of unidentified reaction products/impurities.

EXPERIMENTAL

The syntheses of the *t*-butylaminotriphenylphosphonium trihalides were performed according to the descriptions in our previous studies.[9]

Bromination of Substituted Phenols with t-Butylaminotriphenylphosphonium Tribromide

A typical procedure is given for the synthesis of 4-bromo-3,5-dimethylphenol: To a solution of 3,5-dimethylphenol (0.075 g; 0.6 mmol) in dichloromethane (15 ml)—methanol (2 ml) *t*-butylaminotriphenylphosphonium tribromide (0.3579 g, 0.6 mmol) was added. The mixture was then stirred for 60 min at room temperature. The orange-yellow color of the solution changed to colorless within 1–2 minutes. After the reaction was complete the solvents were evaporated and the remaining residue was extracted repeatedly with ether. The combined ether layers were dried over anhydrous $MgSO_4$ and evaporated to give 4-bromo-3,5-dimethylphenol as colorless needles, recrystallized from methanol-water. m.p.: 113–115°C.

TABLE III

Bromination of phenols with different N-substituted aminotriphenylphosphonium tribromides

Phosphonium Tribromide	4-t-Butyl-phenol	4-Methoxy-phenol	4-Chloro-phenol	4-Nitrophenol
1-Butyl amino	see Table 1	100 % mono	61.4 % mono 18.4 % di [a)] 20.2 % s.m.	0.0 % mono 12.7 % di 87.3 % s.m.
i-Propyl amino	95.2 % mono 1.5 % di 3.3 % s.m.	91.1 % mono 8.9 % di	75.8 % mono 11.6 % di 12.6 % s.m.	0.0 % mono 11.7 % di 88.3 % s.m.
4-Methoxy-anilino	93.0 % mono trace di 7.0 % s.m.	82.1 % mono trace di 17.9 % s.m.	78.8 % mono 8.8 % di 12.4 % s.m.	0.0 % mono 31.8 % di 68.2 % s.m.
Amino	58.3 % mono 0.0 % di 41.7 % s.m.	71.7 % mono 0.0 % di 28.3 % s.m.	55.3 % mono 1.5 % di 43.2 % s.m.	0.0 % mono 9.6 % di 90.4 % s.m.

a) The structure(s) of the dibrominated product(s) in all runs was (were) not determined

Bromination of Substituted Phenols With Bromine

A typical procedure for the synthesis of 2-bromo-3,5-di-*tert*-butylphenol proceeded as follows: To a solution of 3,5-di-*tert*-butylphenol (0.8262 g; 4.0 mmol) in dichloromethane (40 ml) methanol (5 ml) bromine (0.64 g; 4.0 mmol) was slowly added and stirred for 120 min at room temperature. The reaction was terminated by adding an aqueous sodium thiosulfate solution. After repeated extraction with dichloromethane the solutions were combined and dried over anhydrous $MgSO_4$. After evaporation of the solvent 2-bromo-3,5-di-*tert*-butylphenol remained. It was recrystallized from methanol-water.

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