Reactions of Alkylamino- and Dialkylaminotriphenylphosphonium Halides with Halogens and Interhalogen Compounds; Formation of Alkylaminotriphenylphosphonium Polyhalides

Hans Zimmer*, Madhusudan Jayawant, Adel Amer**, and Bruce S. Ault
Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221, USA
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Introduction

In a series of papers we demonstrated the synthetic utility of alkylaminotriphenylphosphonium halides and the corresponding phosphinimines [1a–d]. It was shown that alkyl-[1a] and cycloalkyltriphenylphosphinines could be alkylated with iodomethane or -ethane to the corresponding phosphonium salts which upon hydrolysis gave high yields of secondary amines. Recently this reaction was extended to synthesize arylalkylamines by alkylating arytriphenylphosphinines [2]. In order to further explore the synthetic utility of alkylaminotriphenylphosphonium salts we planned to N-brominate these salts in order to obtain the corresponding N-bromo-N-alkylamino-triphenylphosphonium bromides. It was thought that amination of these salts in analogy to a modified Raschig synthesis [3] would represent a rather convenient way to alkylhydrazines via hydrolysis of the aminated phosphonium salts (eqs (1–3)) [1d].

\[
[Ph_3P-N-alk]Br + Br_2 \rightarrow \frac{\text{H}}{\text{Br}} \quad \text{(1)}
\]

\[
[Ph_3P-N-alk]Br + Br_2 \rightarrow \frac{\text{R}_2NH}{\text{Br}} \quad \text{(2)}
\]

\[
[Ph_3P-N-alk]Br + \text{NR}_2 \rightarrow \frac{\text{NR}_2}{\text{OH}} \quad \text{(3)}
\]

However, instead of N-bromination taking place, polyhalide formation was observed (eq. (4)).

\[
[Ph_3P-NHalk]X + Br_2 \rightarrow \frac{\text{Ph}_3P=0 + R_2N\text{-NHalk}}{\text{(R = alkyl)}} \quad \text{(4)}
\]

While ammonium trihalides have been prepared and studied in some detail, there have been very few reports of the preparation of quaternary phosphonium trihalides [4]. Also, in earlier reports on the synthesis of N-alkyl- and N-dialkylaminotriphenylphosphonium halides and the corresponding aryl analogs, no mention of formation of polyhalides has been made [1, 5-10].

Results and Discussion

To achieve N-bromination the alkylaminotriphenylphosphonium halides were reacted with elemental bromide. It was found that tribromides derived from N-alkylaminotriphenylphosphonium...
cations form with ease when equivalent quantities of halide salts and elemental bromine are reacted in chloroform solution. $t$-Butylamino-isopropylamino- and the unsubstituted aminotriphenylphosphonium cation formed stable tribromides.

Cycloalkylaminotriphenylphosphonium tribromides were rather unstable and decomposed to a certain extent during purification attempts. In the presence of water, triphenylphosphine oxide and the corresponding alkylammonium bromide were the only isolated products [1d] (eq. (5)).

$\begin{align*}
\text{R} &= \Delta, \quad \text{O}, \quad \text{C} \quad \text{CH}_3, \text{C}_2\text{H}_5 \\
[(\text{C}_6\text{H}_5)_3\text{PNHR}]^+\text{Br}_3^- + \text{H}_2\text{O} &\rightarrow (\text{C}_6\text{H}_5)_3\text{P}=\text{O} + \text{H}_2\text{NR} \cdot \text{HBr}
\end{align*}$

The methylamino- and cycloheptylaminotriphenylphosphonium tribromides could not be purified sufficiently for analysis; both yielded after recrystallization only the corresponding alkylaminotriphenylphosphonium bromides, though originally they showed a positive KI-starch-iodine test. In Table I the synthesized tribromides are compiled.

For identification purposes we relied on the results of the elemental analyses, as well as IR- and Raman spectroscopic evidence. In view of the stability of $t$-butylaminotriphenylphosphonium tribromide, other trihalides of the $t$-butylaminotriphenylphosphonium cation were synthesized by applying the method developed for the tribromide formation. Generally it was found that symmetrical trihalides are more stable than unsymmetrical ones. Thus, when $t$-butylaminotriphenylphosphonium iodide was reacted with ICl the expected $\text{I}_2\text{Cl}^-$ salt was formed initially; but during purification by successive crystallization from chloroform-ether mixture, the melting point of the salt rose from $144^\circ$ to $187^\circ$ C, the melting point of pure $t$-butylaminotriphenylphosphonium triiodide. The same behavior was observed on treating the corresponding chloride with elemental iodine; the initially formed $\text{ClI}_2^-$ salt was identical with the first one and during purification attempts it also gave the triiodide. (eq. (6)).

Table I. $[(\text{C}_6\text{H}_5)_3\text{PNHR}]^+\text{Br}_3^- + \text{Br}_2 \rightarrow [(\text{C}_6\text{H}_5)_3\text{PNHR}]^+[(\text{Br}_3)]^\ominus$.

<table>
<thead>
<tr>
<th>No.</th>
<th>R.</th>
<th>Formula</th>
<th>Mol. wt.</th>
<th>M.p. $[^\circ\text{C}]^{\text{a}}$</th>
<th>Yield</th>
<th>Analysis $[^%]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>$\text{C}<em>{18}\text{H}</em>{17}\text{Br}_3\text{NP}$</td>
<td>518.05</td>
<td>157-158$^{\text{b}}$</td>
<td>84.2</td>
<td>2.70</td>
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<tr>
<td>2</td>
<td>$\text{CH}_3$</td>
<td>$\text{C}<em>{19}\text{H}</em>{19}\text{Br}_3\text{NP}$</td>
<td>532.07</td>
<td>107-108$^{\text{c,d}}$</td>
<td>52.1</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>$\text{C}_2\text{H}_5$</td>
<td>$\text{C}<em>{20}\text{H}</em>{21}\text{Br}_3\text{NP}$</td>
<td>546.09</td>
<td>121-122$^{\text{b}}$</td>
<td>71.9</td>
<td>2.56</td>
</tr>
<tr>
<td>4</td>
<td>$t\text{-C}_3\text{H}_7$</td>
<td>$\text{C}<em>{21}\text{H}</em>{23}\text{Br}_3\text{NP}$</td>
<td>560.12</td>
<td>161-162$^{\text{b}}$</td>
<td>89.2</td>
<td>2.50</td>
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<td>$t\text{-C}_4\text{H}_9$</td>
<td>$\text{C}<em>{22}\text{H}</em>{25}\text{Br}_3\text{NP}$</td>
<td>574.15</td>
<td>146$^{\text{b}}$</td>
<td>93.1</td>
<td>2.44</td>
</tr>
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<td>6</td>
<td>$\Delta$</td>
<td>$\text{C}<em>{21}\text{H}</em>{23}\text{Br}_3\text{NP}$</td>
<td>558.11</td>
<td>96-97$^{\text{c}}$</td>
<td>65.4</td>
<td>2.51</td>
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<tr>
<td>7</td>
<td>$\text{C}$</td>
<td>$\text{C}<em>{23}\text{H}</em>{25}\text{Br}_3\text{NP}$</td>
<td>586.16</td>
<td>130-131$^{\text{c}}$</td>
<td>67.7</td>
<td>2.39</td>
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<tr>
<td>8</td>
<td>$\text{O}$</td>
<td>$\text{C}<em>{24}\text{H}</em>{27}\text{Br}_3\text{NP}$</td>
<td>600.19</td>
<td>149-150$^{\text{c}}$</td>
<td>63.2</td>
<td>2.33</td>
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<tr>
<td>9</td>
<td>$\text{O}$</td>
<td>$\text{C}<em>{25}\text{H}</em>{29}\text{Br}_3\text{NP}$</td>
<td>614.21</td>
<td>95-100$^{\text{c,d}}$</td>
<td>52.1</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Melting points are uncorrected; $^b$ crystallized from CHC13/ether; $^c$ crystallized from ethanol/ether; $^d$ compounds decomposed during purification.
If, however, a 1:2 molar ratio of the iodide and ICl was used, the final product isolated was the 
[ClICl]⁺ trihalide. Its formation could be explained by assuming that the originally formed [ClI₂]⁻ anion 
dissociated into Cl⁻ and I₂; a subsequent reaction between the Cl⁻ and ICl led to the isolated 
[(C₆H₅)₃PNHt-C₆H₅][ClICl]. The formation of this salt is in agreement with the fact that mixed 
halide anions with iodine as the central atom are generally fairly stable. Our observation about 
the stability of the trihalides derived of the t-butylaminotriphenylphosphonium cation parallels the 
order of stabilities of alkali metal trihalides established by Ephraim [11]. Other mixed trihalides were 
prepared by reacting halides with interhalogen compounds or halogens as illustrated by the following 
reactions (eqs 7 and 8).

\[
((C₆H₅)₃PNHt-C₆H₅)[I⁺ + Br₂] \rightarrow ((C₆H₅)₃PNHt-C₆H₅)[Br⁺ + IBr] (7)
\]

The polyhalides of the t-butylaminotriphenylphosphonium cations which were prepared during 
this investigation are listed in Table II. The yield in all cases was good to excellent. That trihalide 
formation is not restricted to the N-t-butylnatriomorphylphosphonium cation is shown by successful 
synthesis of a few trihalides derived of other N-alkyl- and N,N-dialkylaminotriphenylphosphonium 
cations (Table III). All products were stable in the solid state and could be kept for years provided 
mucrose was excluded.

Attempts to obtain the desired N-bromo compounds by reacting the triphenyl-t-butylnatriophosphonium brimide with N-bromosuccinimide yielded a rather unstable colorless compound which gave a positive test with KI-starch reagent. Attempts to purify this compound by crystallization or thin-layer chromatography resulted only in formation of 5.

Spectroscopical Investigation

The infrared spectra, in the region 200–4000 cm⁻¹, were similar for all compounds and showed usually 
a rather broad peak in the 3240–3350 cm⁻¹ region

Tab. II. [(C₆H₅)₃PNH-t-C₆H₅]⁺X⁻ + Y₂ → [(C₆H₅)₃PNH-t-C₆H₅]⁺[XY₂]

<table>
<thead>
<tr>
<th>No.</th>
<th>XY₂⁻</th>
<th>Formula</th>
<th>Mol.wt.</th>
<th>M.p. [°C]a,b</th>
<th>Yield</th>
<th>Analyses [％]</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
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<tbody>
<tr>
<td>1</td>
<td>BrCl2</td>
<td>C₂₂H₂₅BrCl₃NP</td>
<td>485.23</td>
<td>144–145</td>
<td>85.2</td>
<td>2.89</td>
<td>41.78</td>
<td>14.61</td>
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<td>8.19</td>
<td>16.47</td>
<td>16.19</td>
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<td>2</td>
<td>ICl₂</td>
<td>C₂₂H₂₅Cl₂INP</td>
<td>532.22</td>
<td>157</td>
<td>84.1</td>
<td>2.63</td>
<td>14.37</td>
<td>13.32</td>
<td>20.43</td>
<td>20.34</td>
<td>23.84</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Br₃</td>
<td>C₂₂H₂₅Br₃NP</td>
<td>574.15</td>
<td>146</td>
<td>93.1</td>
<td>4.39</td>
<td>13.92</td>
<td>41.77</td>
<td>41.78</td>
<td>25.38</td>
<td>20.43</td>
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</tr>
<tr>
<td>4</td>
<td>IBr₂</td>
<td>C₂₂H₂₅Br₂INP</td>
<td>621.14</td>
<td>160</td>
<td>90.2</td>
<td>2.25</td>
<td>25.38</td>
<td>41.78</td>
<td>20.34</td>
<td>25.38</td>
<td>20.43</td>
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<tr>
<td>5</td>
<td>I₃</td>
<td>C₂₂H₂₅I₃NP</td>
<td>715.14</td>
<td>188–189</td>
<td>95.5</td>
<td>3.52</td>
<td>1.96</td>
<td>37.01</td>
<td>3.56</td>
<td>22.01</td>
<td>22.03</td>
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<td>ClIBr</td>
<td>C₂₂H₂₅BrClINP</td>
<td>576.68</td>
<td>160</td>
<td>86.7</td>
<td>2.43</td>
<td>6.15</td>
<td>13.86</td>
<td>22.01</td>
<td>22.01</td>
<td>13.92</td>
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<tr>
<td>7</td>
<td>BrI₂</td>
<td>C₂₂H₂₅BrI₂NP</td>
<td>668.14</td>
<td>170</td>
<td>81.4</td>
<td>2.09</td>
<td>6.08</td>
<td>13.86</td>
<td>22.01</td>
<td>22.01</td>
<td>13.92</td>
<td></td>
</tr>
</tbody>
</table>

a Compounds crystallized from CHCl₃/ether; b melting points are uncorrected.
characteristic of the NH-stretching mode of the cation. For the Raman spectroscopic investigation compounds 1, 3 (Table II) and [Ph₃PNH-t-C₆H₉]Br⁺ [1a] were selected. The Raman spectra of compounds 1 and 3 (Fig. 1), in the low frequency region responding to the first overtone of the symmetric stretching mode, indicating some resonance enhancement of the signal. The Raman spectrum of the BrCl₂⁺ salt showed two weaks lines, at 163 and 275 cm⁻¹ while the Br⁺ salt showed no Raman lines in the low energy region. The Raman spectra strongly thus support the existence of the trihalide anions in these salts.

The Raman spectra also provide some information as to the local environment of the anion. For Br₃⁺, an intense Raman line was observed for ν₁, the symmetric stretching mode, while no hint of a line was observed near 190 cm⁻¹, where ν₂, the antisymmetric stretching mode should be observed. This mode is Raman inactive [13] if the anion maintains a center of symmetry, but should be activated if the anion is distinctly perturbed in the crystal. The Raman spectrum of the BrCl₂⁺ salt was less intense, and somewhat less definitive, showing lines at 163 and 275 cm⁻¹. The upper line is in good agreement with the symmetric stretching mode of the centrosymmetric BrCl₂⁺ anion, but again only one vibrational mode is anticipated for this species. The Raman line at 163 cm⁻¹ may indicate that the anion is not centrosymmetric, but distorted or even chlorine-centered, BrClCl⁺; this species should have Raman stretching modes in both of these spectral regions. Alternatively, the 163 cm⁻¹ line might be attributed to a small amount of Br₃⁺ impurity.

Further support for lack of N-bromination but formation of trihalide anions instead during these reactions comes from ³¹P-investigations of [Ph₃P-NHC(CH₃)₃]Br⁺ and compounds 1 (Table II). The observed values were δ —31.156 and —31.196 with H₃PO₄ as external standard. These values are

---

### Table III.

<table>
<thead>
<tr>
<th>No.</th>
<th>R₁</th>
<th>R₂</th>
<th>XY₂⁻</th>
<th>Formula</th>
<th>Mol.wt.</th>
<th>M.p. [°C]¹,b</th>
<th>Yield</th>
<th>Analyses [%] N Calculated Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(CH₃)₂CH</td>
<td>H</td>
<td>BrI₂</td>
<td>C₂₃H₂₃Br₂NP</td>
<td>654.11</td>
<td>142-143b</td>
<td>92.3</td>
<td>2.14</td>
</tr>
<tr>
<td>2</td>
<td>CH₃</td>
<td>(CH₃)₂C</td>
<td>IBr₂</td>
<td>C₂₃H₂₇Br₂INP</td>
<td>635.17</td>
<td>167</td>
<td>90.5</td>
<td>2.20</td>
</tr>
<tr>
<td>3</td>
<td>CH₃</td>
<td>(CH₃)₂C</td>
<td>I₃</td>
<td>C₂₃H₂₇I₃NP</td>
<td>729.17</td>
<td>209-210</td>
<td>93.0</td>
<td>1.92</td>
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</table>

¹ Melting points are uncorrected; ² crystallized from CHCl₃/ether.
well in the range of $^{31}$P chemical shifts of aminotriphenylphosphonium salts [14], thus showing that no structural changes in close proximity of the P-atom occurred.

**Experimental**

Infrared spectra were recorded in Nujol mulls on a Beckman IR-12 infrared spectrophotometer, while Raman spectra were taken of the powdered material in capillary tubes. These spectra were recorded on a Spex Ramalog spectrometer, after excitation by either the 4880 Å or the 5145 Å line of an argon laser (Coherent Radiation). Slight decomposition of the Br$_3$ and BrCl$_2$ salts was observed when 5145 Å excitation was employed, and considerable decomposition was noticed when the 4880 Å line was used. The BrCl$_2$ was particularly susceptible to decomposition, and consequently less intense Raman lines were obtained. The $^{31}$P NMR spectra were obtained with a Bruker HX-90 model in DMSO-d$_6$ solution.

Melting points were uncorrected. The micro-analyses were done by Galbraith Laboratories, Knoxville, TN.

**Alkyl- and cycloalkylaminotriphenylphosphonium tribromides- general procedure**

To a magnetically stirred, ice-cold solution of cycloalkyl or alkylaminotriphenylphosphonium bromide in chloroform an equimolar 10% solution of bromine in chloroform was added dropwise. Temperature was not allowed to exceed 10 °C during addition and an inert atmosphere was maintained over the reaction mixture. When the reaction was over, chloroform was evaporated at temperatures below 50 °C and the residue was triturated with dry ether. In the cases of low melting solids, an orange viscous oil was obtained after removal of the solvent and this was triturated with ether.

**Aminotriphenylphosphonium tribromide and ethyl-, isopropyl- or $t$-butylaminotriphenylphosphonium tribromides** were precipitated directly from chloroform solutions by addition of dry ether. They were purified by crystallization from chloroform-ether.

In case of methyl-, cyclopropyl-, cyclopentyl-, cyclohexyl-, and cycloheptyl-aminotriphenylphosphonium tribromides, however, chloroform was removed as completely as possible before crystallization either from ethanol or from ethanol-ether mixtures was attempted. Crystallizations of these compounds proceeded very slowly and decomposition to the corresponding phosphonium bromides or the primary amine hydrobromides plus triphenylphosphine oxide was extensive.

**$t$-Butylaminotriphenylphosphonium polyhalides; general procedure:** These polyhalides were synthesized according to the above procedure. The following halogens or interhalogen compounds were used for the reaction with $t$-butylaminotriphenylphosphonium chloride, bromide or iodide: Cl$_2$, Br$_2$, I$_2$, ICl, and IBr. Reactions with chlorine were carried out by bubbling a slow stream of dry chlorine gas into an ice-cold 10% solution of the appropriate phosphonium halide in chloroform. The amount of chlorine absorbed was measured by gain in weight. The trichloride decomposed readily. Secondary reactions observed in the case of $t$-butylaminotriphenylphosphonium iodide – iodine monochloride, and $t$-butylaminotriphenylphosphonium iodide – chlorine reactions were the result of increased proportions of halogen or interhalogen compounds. They are described in the discussion section.

**N,N-Dialkylamino- and i-propylaminotriphenylphosphonium polyhalides Table III:** Conditions as above were used to react N-methyl,N-$t$-butylaminotriphenylphosphonium iodide with bromine or iodine and of isopropylaminotriphenylphosphonium bromide with iodine. To the reaction mixture in chloroform, 50 ml dry ether was added to precipitate the corresponding polyhalides, which were filtered off, dried and purified by recrystallization.

\[1\] a) H. Zimmer and G. J. Singh, Org. Chem. 28, 483 (1963);
c) H. Zimmer and G. Singh, J. Org. Chem. 29, 3412 (1964);


b) D. Kanai, T. Hashimoto, H. Kitano, and K. Fukui, Nippon Kagaku Zaashi 86, 534 (1963);
C. A. 63, 6586c (1965);


