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Syntheses and Crystal Structures of Phosphonium Bromides

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As part of our studies on the crystal structures of phosphonium halides [1] we have prepared various phosphonium bromides. These can be obtained by the reaction of a phosphine with aryl or alkyl bromides in acetonitrile or methylene chloride:

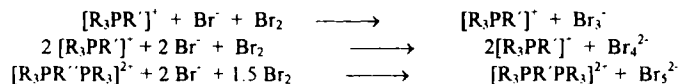


R = Me₃N, Et₃N, Pr₃N; Bu₃N; R' = CH₂-C₆H₅
 R = C₆H₅; R' = CH₂-C₆H₄Br



R = C₆H₅; R'' = CH₂; C₂H₄

The polybromides have been obtained by treating the simple bromides with corresponding molar quantities of bromine in the same solvents:



All these phosphonium bromides consist of discrete monomeric phosphonium cations and bromide or polybromide anions.

As expected, the various cations have a nearly tetrahedral geometry around the P atoms. They show no special features with exception of the tris(dialkyl-amino)benzylphosphonium bromides. In these compounds, the N atoms of the cations are nearly trigonal planar configured.

The (p-bromobenzyl)triphenylphosphonium dibromide consists of corresponding phosphonium cations and in contrast to [2,3] isolated linear Br₃²⁻ anions.

The blue crystals of methylene bis(triphenylphosphonium) pentabromide and ethylene bis(triphenylphosphonium) tetrabromide consist of isolated cations and tetrahedral Br₅²⁻ and trigonal pyramidal Br₄²⁻ anions, respectively. These two anions are the first examples of spheric polybromide anions.

References

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