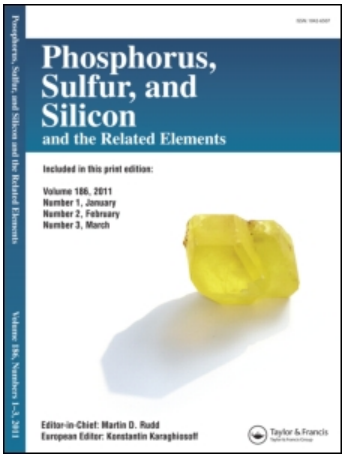

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Synthesis and Crystal Structure of Halomethyltriphenylphosphonium Halides and Bromotriphenylphosphonium Tribromide

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SYNTHESIS AND CRYSTAL STRUCTURE OF HALOMETHYLTRIPHENYLPHOSPHONIUM HALIDES AND BROMOTRIPHENYLPHOSPHONIUM TRIBROMIDE

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The phosphonium salts have been prepared by the reaction of triphenylphosphine with the corresponding halomethanes (eq. (1)) and bromine (eq.(2)), respectively.

$$(C_6H_5)_3P + RX \longrightarrow [(C_6H_5)_3PR]^+ X^- \quad (1)$$

[R = CH_2I X = I (**I**); R = CBr_3 X = Br, (**II**); R = CBr_3 X = Br; Br_3 (**III**); R = CH_2Br X = Br_3 (**IV**)]

$$(C_6H_5)_3P + 2\,Br_2 \longrightarrow [(C_6H_5)_3PBr]^+ Br_3^- \text{ (V)} \quad (2)$$

The crystal and molecular structures of **I - V** have been determined by X-ray structure analysis. The crystals are orthorhombic ($Pca2_1$ (**I**)), triclinic ($P\bar{1}$ (**II**)), and monoclinic (C2/c (**III**); $P2_1/n$ (**IV**); $P2_1/c$ (**V**)). In the solid state all compounds consist of discrete monomeric $(C_6H_5)_3PR^+$ cations and X^- anions with halogen halogen interactions between the halogens bonded in the cations and the halogen anions. The cations of **I - V** have a slightly irregular tetrahedral geometry around the P atom. The Br_3^- anions are nearly linear with symmetrical (**III**) or asymmetrical (**IV, V**) Br Br bonding distances.

(**I**) is the first compound in which a iodine atom bonded to carbon interacts with the iodide anion. The Br Br interactions lead to formation of rings (**II**), chains (**III**), and dimeric units (**IV**).