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## Phosphorus, Sulfur, and Silicon and the Related Elements

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### Synthesis and Crystal Structure of Halomethyltriphenylphosphonium Halides and Bromotriphenylphosphonium Tribromide

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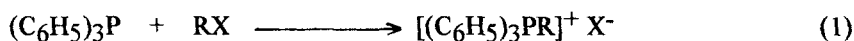
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## SYNTHESIS AND CRYSTAL STRUCTURE OF HALOMETHYLTRI-PHENYLPHOSPHONIUM HALIDES AND BROMOTRIPHENYL-PHOSPHONIUM TRIBROMIDE

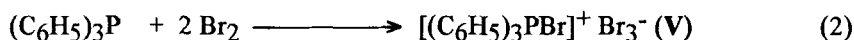
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The phosphonium salts have been prepared by the reaction of triphenylphosphine with the corresponding halomethanes (eq. (1)) and bromine (eq.(2)), respectively.



[R = CH<sub>2</sub>I X = I (I); R = CBr<sub>3</sub> X = Br, (II); R = CBr<sub>3</sub> X = Br; Br<sub>3</sub> (III); R = CH<sub>2</sub>Br X = Br<sub>3</sub> (IV)]



The crystal and molecular structures of I - V have been determined by X-ray structure analysis. The crystals are orthorhombic (Pca2<sub>1</sub> (I)), triclinic P $\bar{1}$  (II), and monoclinic (C2/c (III); P2<sub>1</sub>/n (IV); P2<sub>1</sub>/c (V)). In the solid state all compounds consist of discrete monomeric (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PR<sup>+</sup> cations and X<sup>-</sup> 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<sub>3</sub><sup>-</sup> 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).