



Oxidation of tris(2,4,6-triisopropylphenyl)phosphine and arsine



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ABSTRACT

A reaction of the radical cation of tris(2,4,6-triisopropylphenyl)phosphine with oxygen gave a phosphonium salt resulting from the introduction of the oxygen atom to the phosphorus and the formation of a five membered ring by participation of the *ortho* isopropyl group. On the other hand, oxidation of the phosphine with *m*CPBA afforded the corresponding phosphine oxide. X-ray crystallography showed that the C–P–C bond angles and the P–C bond lengths of the phosphine oxide are similar to those of the corresponding phosphine. The corresponding arsine underwent analogous reactions to afford the arsonium salt and the arsine oxide.

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Triarylphosphines are one of the most common phosphorus compounds in the laboratory and are regarded as precursors for various synthetically important compounds such as phosphonium salts, phosphoranes, iminophosphoranes, phosphine oxides, phosphine sulfides, and metal phosphine complexes. We have been involved in the synthetic study of the sterically crowded triarylphosphines during the last decade.¹ Typical sterically crowded triarylphosphines such as trimesitylphosphine,² tris(2,4,6-triisopropylphenyl)phosphine (**1a**),³ and tris(2,6-diisopropylphenyl)phosphine⁴ are reversibly oxidized at low potentials to give stable radical cations because of the synergistic effect of the high HOMOs resulting from the structural change around the phosphorus atom and the steric protection by the bulky substituents (Chart 1). The arsenic and antimony counterparts such as **1b** also show similar structural characteristics and redox properties.³ We have also synthesized sterically crowded triarylphosphines similar to **1a** bearing donors,⁵ acceptors,⁶ and radicals⁷ to demonstrate that these structures can be potential candidates for the key structures of functional materials. On the other hand, conventional derivatives of **1a** and the related compounds have not yet been reported except for radical cation **1a**^{•+},^{3,4,8} and phosphonium salt **1aH**⁶⁺. The previous attempts to synthesize the phosphine oxide of **1a** by us³ and that of tris(2,6-diisopropylphenyl)phosphine by Boeré et al.,⁴ by oxidation with hydrogen peroxide resulted in

the recovery of the phosphine. Because **1a** has the largest bond angles and the longest bond lengths around the phosphorus atom, and the lowest oxidation potential among the triarylphosphines we surveyed, derivatives such as the phosphine oxide inevitably have very crowded structures of interest. Thus, we have been continuing studies on the synthesis of the derivatives of sterically crowded triarylphosphines, and have found the unique reactivity of **1a**. We herein report the oxidation and the structures of the oxygenated derivatives of **1a** and the corresponding arsine **1b**. Sterically crowded triarylphosphine **1a** and arsine **1b** give different oxygenated products depending on the way of oxidation. One electron oxidation of **1a** and **1b** followed by reaction with oxygen leads to the introduction of oxygen to the pnictogen and participation of the *ortho* isopropyl group. On the other hand, oxidation of **1a** and **1b** with *m*CPBA gives conventional oxides.

Triarylphosphine **1a** and arsine **1b** can be oxidized to the corresponding radical cations chemically with various oxidants such as AgClO₄ and tris(4-bromophenyl)aminium perchlorate as well as electrochemically.³ It should be noted that the preparation of radical cation **1a**^{•+} with oxidants such as AgClO₄ suffered from

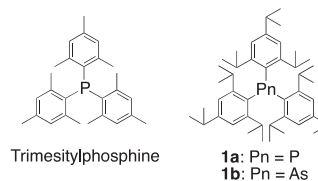


Chart 1. Sterically crowded triarylphosphine and arsine.

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the competitive formation of phosphonium cation **1aH**⁺ because of the basicity of the phosphine and unavoidable acidic impurities, and, thus, the reaction was sensitive to moisture. Phosphonium cation **1aH**⁺ can be alternatively generated by protonation of **1a** by trifluoroacetic acid in CDCl₃ or dichloromethane, and the disappearance of **1a** and the formation of **1aH**⁺·CF₃CO₂⁻ were confirmed by NMR and UV–vis spectroscopy (**1aH**⁺·CF₃CO₂⁻: ³¹P NMR (CF₃CO₂H/CDCl₃) δ -31.32 (d, J = 479.9 Hz); UV–vis (CF₃CO₂H/dichloromethane) λ_{max}(ε)/nm 289 (6310), 281 (6540), 246 (53500)). On the other hand, the less basic arsenic atom of **1b** was not protonated under similar conditions and the oxidation of **1b** to the radical cation was less sensitive to moisture than **1a**. The UV absorption characteristic of **1b** (λ_{max}(ε) 295 (14300) nm) was not affected by the addition of trifluoroacetic acid in dichloromethane and the NMR spectral changes were limited to those resulting from the interaction between the aromatic ring and trifluoroacetic acid. Radical cations **1a**^{•+} and **1b**^{•+} exhibit an intense purple color and characteristic UV–vis absorptions (λ_{max}/nm 527, 479sh, 383, 366, 281sh, 241 (**1a**^{•+}·ClO₄⁻); 517, 360, 277, 228 (**1b**^{•+}·ClO₄⁻)) were consistent with the previous reports (Fig. 1)2780.^{3,4,8} The similarity of the UV–vis spectra of the radical cations of the triarylphosphine, arsine, and amines⁹ suggests analogous electronic structures.

One electron oxidation of triarylphosphine to the corresponding radical cation followed by the reaction with molecular oxygen has been reported to give triarylphosphine oxide as a final product.¹⁰ However, generation of the radical cation of **1a** and the following reaction with oxygen did not give the corresponding phosphine oxide. The oxidation of **1a** with AgClO₄ under an oxygen atmosphere gave a dark purple mixture of the radical cation, and the mixture turned nearly colorless in 30 min and the ³¹P NMR spectrum of the mixture showed only two peaks (δ 73.4 (s) and -30.7 (d, J_{PH} = 494.4 Hz)), although the ratio was dependent on the conditions such as dryness of the solvent and the oxidant (Scheme 1). The latter is phosphonium **1aH**⁺ generated by protonation with HClO₄ and surviving oxidation. The former was purified by column chromatography and recrystallization, and assigned as phosphonium salt **2a**·ClO₄⁻. The oxidation of **1a** with AgClO₄ under an argon atmosphere followed by the introduction of oxygen or air gave the same products, and the aerobic oxidation of **1a** in dichloromethane was very slow. Thus, **2a**·ClO₄⁻ was regarded to be a product resulting from the reaction of **1a**^{•+} with oxygen. The UV–vis spectra of **1a**^{•+}·ClO₄⁻, generated by the oxidation of **1a** with AgClO₄ in dichloromethane, also showed the conversion of **1a**^{•+}·ClO₄⁻ to **2a**·ClO₄⁻ upon exposure to air. The disappearance of the absorptions characteristic of **1a**^{•+}·ClO₄⁻ and the growth of the absorptions corresponding to **2a**·ClO₄⁻ were observed (Fig. 1).

The structure of **2a** was determined by spectroscopic methods. The mass spectrum shows a parent peak of phosphonium **2a** and weak peaks corresponding to the remaining by-products arising from the incorporation of oxygen atoms to the substituents (FT-ICR-MS (ESI) *m/z* 655.50021 (100%) calcd for [C₄₅H₆₈OP]⁺, 655.50023; 671.49529 (6%), calcd for [C₄₅H₆₈O₂P]⁺, 671.49514; 687.49022 (5%), calcd for [C₄₅H₆₈O₃P]⁺, 687.49006). The ¹H and ¹³C NMR spectra in CDCl₃ show a frozen and unsymmetrical structure, where all carbons and the corresponding protons are nonequivalent except for accidental overlap. The three *ipso* aryl carbons with the large J_{PC} typical of the compounds such as phosphonium salts and phosphine oxides¹¹ (δ 127.33 (d, J_{PC} = 99.86 Hz, Tip1-1), 120.41 (d, J_{PC} = 86.59 Hz, Ar-1), 117.44 (d, J_{PC} = 99.87 Hz, Tip2-1)) support the presence of the three aryl groups on the phosphorus atom and exclude rearrangement of the aryl group to the oxygen atom. A quaternary carbon connected to the oxygen was observed at low field (δ 95.92, (J_{PC} = 1.37 Hz)). The loss of one methine proton and the HMBC correlation of the quaternary carbon with two methyl group protons, the two singlet signals at δ 1.881 and 1.262, support the introduction of an oxygen atom to

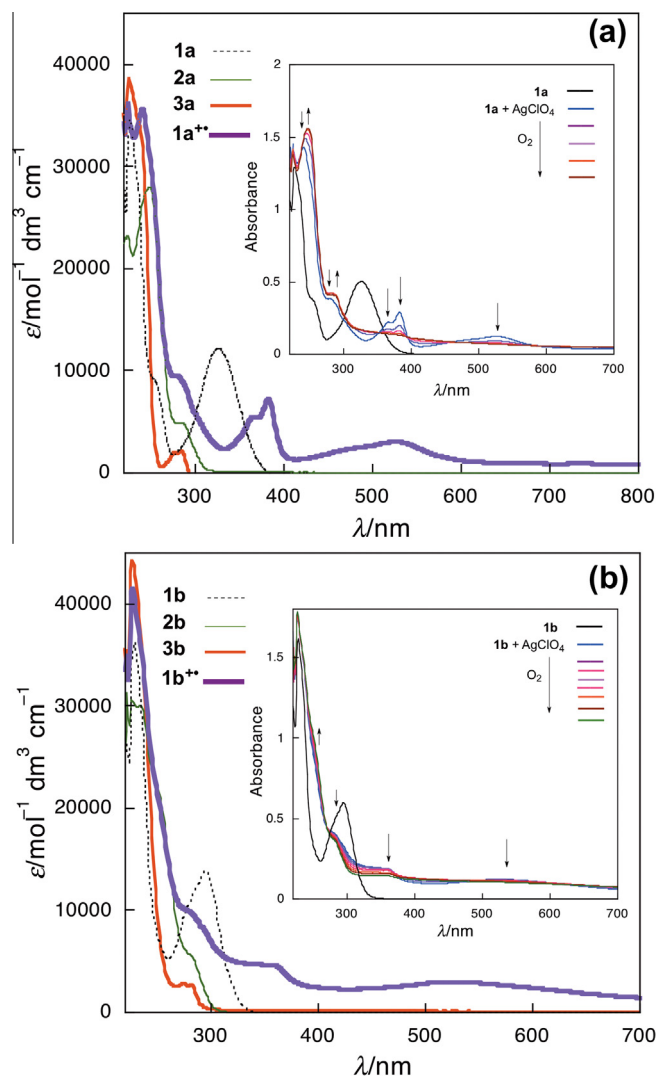
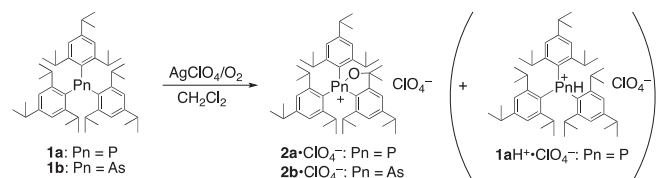


Figure 1. (a) UV–vis spectra of triarylphosphine **1a**, phosphonium **2a**·ClO₄⁻, and phosphine oxide **3a** in dichloromethane, and radical cation **1a**^{•+}·ClO₄⁻ obtained by the addition of AgClO₄ to a dichloromethane solution of **1a**. Inset: UV–vis spectral change of triarylphosphine **1a** after the addition of AgClO₄ in air. (b) UV–vis spectra of triarylar sine **1b**, arsonium **2b**·ClO₄⁻, and arsine oxide **3b** in dichloromethane, and radical cation **1b**^{•+}·ClO₄⁻ obtained by the addition of AgClO₄ to a dichloromethane solution of **1b**. Inset: UV–vis spectral change of triarylar sine **1b** after the addition of AgClO₄ in air. The intensity of the spectra of the radical cations is normalized to the concentration of the neutral precursor, although the spectra suffer from contamination by **2a** and **1aH**⁺ or **2b** (see text) as well as high baselines due to impurities derived from the oxidant.



Scheme 1. Reaction of radical cations of tris(2,4,6-triisopropylphenyl)phosphine (**1a**) and arsine (**1b**) with oxygen.

the *ortho*-isopropyl group. The down-fielded ³¹P NMR chemical shift (δ 74.25 in CDCl₃) suggests specific interaction such as intramolecular hydrogen bonding to a phosphine oxide or the formation of a phosphonium salt, and excludes penta-coordinated phosphorus. The infrared absorptions corresponding to P=O or P–O stretching were overlapped with the strong absorption of the

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