Bromine–Triphenyl Phosphite

\[
\text{Br}_2·\text{P(OPh)}_3
\]

**Br2·P(OPh)3**

[76934-05-9] C18H15Br2O3P (MW 470.10)

InChI = 1/C18H15O3P.Br2/c1-4-10-16(11-5-1)19-22(20-17-12-6-2-7-13-17)21-18-14-8-3-9-15-18-1-2/h1-15H

InChIKey = QYFXVFIXMGYHEN-UHFFFAOYAK

(1)

**InChI**

InChI = 1/C18H15O3P/c1-4-10-16(11-5-1)19-22(20-17-12-6-2-7-13-17)21-18-14-8-3-9-15-18-1-2/h1-15H

(2)

**InChIKey**

InChIKey = GDTBXPJZTBHREO-UHFFFAOYAY

[101-02-0] C18H15O3P (MW 310.29)

InChI = 1/Br2/c1-2

InChIKey = HVLLSGMXQDNUAL-UHFFFAOYAF

(3)

**Alternate Names:** bromotriphenylphosphonium bromide; triphenylphosphite dibromide; dibromotriphenylphosphorane.

**Physical Data:**

Br2: mp –7.2 °C; bp 59.5 °C; d^25^ 1.023 g cm\(^{-3}\). (PhO)3P: mp ca. 25 °C; bp 360 °C; d^20^ 1.1844 g cm\(^{-3}\); n^D^ 1.590.

**Solubility:** Br2: sol H2O (0.214 M L\(^{-1}\)); very sol alcohol, ether, CHCl3, CCl4, CS2. (PhO)3P: insol H2O; dec in hot H2O; sol usual organic solvents.

**Form Supplied In:** not available in final form ‘Br2P(OPh)3’. Prepared in situ. The starting materials, Br2 and (PhO)3P, are both widely available; Br2: dark red diatomic liquid; purity >99.5%; (PhO)3P: liquid which solidifies in the cold; purity >97%; typical impurities: (PhO)3PO, PhOH.

**Analysis of Reagent Purity:** 31P NMR δ: Br \(\text{BrP}^+\) (OPh3) \(+4 ± 0.5\); (PhO)3P+128 ± 1; (PhO)3PO=P=O \(-18 ± 0.5\).

**Preparative Methods:** the reagent is mainly prepared in situ or precipitated and washed just before use.

**Handling, Storage, and Precautions:** ‘Br2P(OPh)3’ is very hygroscopic and corrosive. Br2 is a corrosive liquid with a suffocating odor which vaporizes rapidly at rt. (PhO)3P is harmful as a solid or liquid, is an irritant and is moisture sensitive; store in a cool dry place. This reagent should be handled in a fume hood.

**Synthesis of Alkyl Bromides from Alcohols.** Alkyl bromides are prepared conveniently and in good yield from saturated alcohols, either by adding bromine to a mixture of the alcohol and triphenyl phosphite (eq 1) or by first preparing the triphenyl phosphite dibromide and then adding the alcohol (as in eq 3).

\[
\text{Ph}_{3}P + \text{ROH} \quad \downarrow \quad \text{Br}_2 \quad \downarrow \quad 0^\circ \text{C} \quad \text{then} \quad \downarrow \quad \text{rt} \quad \text{BrBr} + \text{OPh}_3P + \text{HBr} \quad (1)
\]

In the preparation of optically active \((-\)-2-Bromo-3-methylbutane from \((+)-3\)-methylbutan-2-ol (eq 2) without rearrangement, \(\text{PhO}_3\text{PBr}_2\) proved to be less effective than \text{Triphenylphosphine–Carbon Tetra} bromide and particularly inferior compared to \text{Triphenylphosphine Dibromide} despite a better overall yield (eq 2).

\[
\begin{array}{c}
\text{Ph}_3P + \text{Br}_2 \quad -15^\circ \text{C} \quad \text{then} \quad \text{rt} \quad \downarrow \quad \text{Ph}_3\text{PBr}_2 \quad + \quad \text{CH}_3\text{Me} \quad (2)
\end{array}
\]

Unsaturated alkenic, alkynic and allenic alcohols are converted into bromides by treating an equimolar mixture of each of them and pyridine with the previously generated \(\text{PhO}_3\text{PBr}_2\) reagent (eq 3). This procedure avoids the addition of \(\text{Br}_2\) and HBr to multiple bonds present in the substrate; \(\text{Br}_2\) reacts first with the phosphite alone and pyridine acts as HBr scavenger. This method gives improved and more consistent yields (37%–76%) and purer products than the conventional \(\text{PB}3\) procedure.

\[
\begin{array}{c}
\text{Ph}_3P + \text{Br}_2 \quad \text{py} \quad -10^\circ \text{C} \quad \text{then} \quad \text{rt} \quad 3 \text{ h} \quad \downarrow \quad \text{Br} \quad (3)
\end{array}
\]

This reagent can also be used to convert hydroxy groups into bromides in carbohydrates and nucleosides. Carbon skeletal rearrangement is observed with hindered compounds such as the protected glucose (1) from which the 6-bromo derivative (2) is obtained instead of the expected 3-bromo derivative (eq 4). In all cases tested the migration of the hydroxy protecting group proceeds with retention of configuration. In spite of low yields, this reaction offers a new route to deoxy sugars after hydrogenolysis of the bromide intermediate.

In the nucleoside field, a double activation has been performed, probably via the C-6-oxyphosphonium species, to give in one pot both a 5’-bromide and 6-phenylthioether (eq 5).

\[
\text{Ph}_3\text{PBr}_2\] effects also such conversions, but in some cases the removal of the OPPh3 byproduct is problematic. This observation is quite general in the use of these reagents: the disadvantages of the bromide intermediate.

Avoid Skin Contact with All Reagents
Synthesis of Aryl Bromides.5 Thermolysis of the tetraphenoxyphosphonium bromide obtained4b from (PhO)3P (2 parts) and Br2 (eq 6) provides bromobenzene (eq 7). Other aryl bromides are also produced from (PhO)3P + OAr′Br−obtained by reacting Ar′OH with (PhO)3PBr2 (Ar′Br yields: Ar′ = 4-NO2C6H4, 82%; 4-ClC6H4, 45%; 4-MeC6H4, 51%).

$2 \text{ (PhO)}_3\text{P} \xrightarrow{\text{Br}_2, 0 \degree \text{C}} \text{ (PhO)}_3\text{PBr} + \text{ (PhO)}_2\text{PBr}$ (6)

$\text{ (PhO)}_4\text{PBr} \xrightarrow{250 \degree \text{C}} \text{ PhBr} + \text{ (PhO)}_3\text{PO}$ (7)

Synthesis of 1,1-Dibromoalkanes. Aliphatic and aromatic aldehydes6 are converted into 1,1-dibromoalkyl derivatives using the (PhO)3PBr2 reagent with moderate to good yields (50–91%) (eq 8).

$\text{R} = \text{c-C}_3\text{H}_7, 70%'; \text{MePhCH}, 56%; \text{Cy}, 55%'; \text{t-Bu}, 50%'; \text{BnOCH}_2, 64%; \text{Ph}, 64%; \text{3-O}_2\text{N-4-Cl-C}_6\text{H}_4, 91%'; (\text{S})\text{-Me(OBn)CH}, 62%$

The use of this reagent is limited since substrates which are sensitive to Lewis acids, such as furfural, acrolein, and O-isopropylideneglyceraldehyde, undergo decomposition under these conditions; however, chiral (S)-2-benzyloxypropionaldehyde could be converted into the dibromo derivative without noticeable racemization.

2. The reactive entity, the addition compound of the halogen and the phosphite, is in fact a mixture of several phosphorus species in equilibrium. The ratio of each component depends on the reaction conditions (solvent, temperature, sense of the addition, etc.) as unequivocally shown by physical measurements:δ 31P NMR clearly indicates the ionic tetracovalent nature of the phosphorus in (PhO)3P+Br− (δ 31P = +4 ± 0.5 ppm).