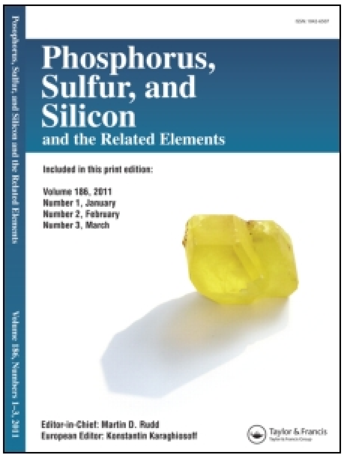

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Communication

A CONVENIENT SYNTHESIS OF ALKYLPHOSPHONIUM SALTS

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The reaction of methanol and its homologs with Ph_3P in 48% aqueous hydrobromic acid provides alkyltriphenylphosphonium salts in quantitative yields.

Key words: Alkylphosphonium salts; alcohols; phosphine aqueous hydrobromic acid.

Triphenylalkylphosphonium salts are generally prepared from triphenylphosphine and alkylbromides or chlorides.[1] The triphenylphosphine hydrobromide proved to be superior to triphenylphosphine in its reactivity towards alkyl chlorides.[2]

It has also been shown that it is possible to prepare phosphonium salts, by reaction of alcohols with triphenylphosphine hydrobromide in organic solvents. Only some particular alcohols such as benzylic or allylic react with triphenylphosphine and aqueous hydrohalide acids to give the corresponding phosphonium salt.[3]

We have found that less reactive alcohols **1** such as methanol and ethanol, under particular conditions, also would react with triphenylphosphine and hydrobromic acid to afford alkyltriphenylphosphonium salts **3** in quantitative yields. This process is also available for *n*-propanol and *n*-butanol (Table I).

We propose the intermediate formation of the alkyl bromide **2**. We observed that the reaction of methanol and triphenylphosphine in the presence of concentrated hydrochloric acid fails to give the phosphonium salt **3**.

$$Ph_3P + HBr \rightarrow Ph_3PHBr^-$$

$$Br^- + \underset{\mathbf{1}}{RCH_2OH} \rightarrow \underset{\mathbf{2}}{RCH_2Br} + Ph_3P \rightarrow \underset{\mathbf{3}}{Ph_3P^+{-}CH_2RBr^-}$$

TABLE I

Synthesis of alkylphosphonium salts **3**. $Ph_3P^+{-}CH_2R, Br^-$

R	Reaction time (h)	Yield (%)	mp (°C)	Lit. data
3a H	15	97	230–233	227–229[4]
3b CH_3	48	97	204–206	206.5–207.5[5]
3c C_2H_5	48	96	232–234	235–238[6]
3d n-C_3H_7	48	97	240–242	241–243[7]

Methyltriphenylphosphonium bromide **3a**. A 250 mL, round bottomed flask fitted with an efficient reflux condenser is charged with triphenylphosphine (26.2 g, 0.1 mol), methanol (12 mL, 0.3 mol), and 48% aqueous hydrobromic acid (58 mL, 0.5 mol). The mixture is heated to 110°C and kept at this temperature for 15 h. The solution is cooled and extracted with $CHCl_3$ (4 × 50 mL). The combined organic phase is dried (Na_2SO_4). The solvent is removed; the first fraction (100 mL) at atmospheric pressure (H_2O—$CHCl_3$), and the residual chloroform at reduced pressure with a rotary evaporator.

The residue is washed with toluene (50 mL) to remove traces of chloroform and Ph_3P. The reaction product is dissolved in the minimum amount of methanol (22 mL), then the solution is diluted with EtOAc (220 mL) and cooled to 0°C to give the salt **3a**. Yield: 34.6 g (97%); m.p. 230–233°C; (Lit.$^{(4)}$ m.p. 232–233°C).

Salts **3b, 3c, 3d**. A 250 mL, round bottomed flask equipped with a reflux condenser is charged with triphenylphosphine (26.2 g, 0.1 mol), alcohol (0.4 mol) and 48% aqueous hydrobromic acid (58 mL, 0.5 mol). The mixture is stirred and heated at 110°C for 48 h. The solution is cooled and extracted with $CHCl_3$ (4 × 50 mL).

The combined extracts are dried (Na_2SO_4) and the solvent is removed *in vacuo*.

The salt is washed with EtOAc (50 mL) to remove traces of Ph_3P and chloroform

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