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# MICROWAVE-ASSISTED SYNTHESIS OF TRIARYL PHOSPHATES

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## MICROWAVE-ASSISTED SYNTHESIS
## OF TRIARYL PHOSPHATES

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Triaryl phosphates are of considerable interest because of their utility as plasticizers, flame retardants, lubricating oil additives and hydraulic fluids.[1] They are synthesized by reaction of phosphoryl chloride with phenols at elevated temperature (160-250°) in the presence of a Lewis acid catalyst,[2] at room temperature using a phase transfer catalyst[3] or by using polymer supported phenoxides.[4] Patented procedures are also available in the literature[5,6] for the synthesis of triaryl phosphates. Some of the reported methods have limitations such as (i) drastic reaction conditions,[2] (ii) liberation of hydrogen chloride which may cause corrosion problems in industrial reactors, (iii) tedious work-up, and (iv) long reaction times. In certain cases, pyridine or dialkylanilines have been used to neutralize the liberated hydrogen chloride. High temperatures often lead to many by-products. Plasticizer grade triaryl phosphates must be of very high purity and the products obtained have to be distilled at low pressure for purification. Distillation at low pressures on an industrial scale raises serious problems.

Therefore, there is need of a rapid and environmentally-friendly general method for the synthesis of triaryl phosphates. In recent years, there has been considerable interest in microwave-induced reactions in organic synthesis.[7,8] In view of the potential applications of triaryl phosphates and substantial reduction in reaction times under microwaves, we now report a novel method for the phosphorylation of phenols.

Triaryl phosphates have been synthesized in excellent yields by reacting phosphoryl chloride with a mixture of sodium hydroxide, few drops of water, and phenol under focused microwaves. Heating reaction mixture for 2-2.5 min followed by cooling was carried out at intervals of 30 sec. At room temperature, the reaction was very slow and incomplete after 5-6 hrs.

$$\underset{\mathbf{1}}{3\mathrm{ArOH}} + \underset{\mathbf{2}}{\mathrm{POCl_3}} \xrightarrow[\text{MW, 2 - 2.5 min}]{\text{NaOH, } H_2O} \underset{\mathbf{3}}{(\mathrm{ArO})_3\mathrm{P{=}O}} + 3\mathrm{NaCl}$$

It is important to note that the reactions are carried out without solvent and there is no need of a catalyst as well as an inert atmosphere for this methodology. This method seems to be advantageous over conventional methods in terms of high yields, pure products, rapid reaction rates and an environmentally friendly procedure.

**Table**. Synthesis of Triaryl Phosphates using Focused Microwaves

| Product | Ar | Time (min.) | mp. (bp.) (°C) | *lit.*[1,9] mp (bp.) | Yield[a,b] (%) |
|---|---|---|---|---|---|
| **3a** | $C_6H_5$ | 2.0 | 49-50 | 49-51 | 90 |
| **3b** | *o*-$MeC_6H_4$ | 2.5 | 90-91 | 90-91 | 88 |
| **3c** | *m*-$MeC_6H_4$ | 2.5 | (257-262) | (258-263) | 87 |
| **3d** | *p*-$MeC_6H_4$ | 2.5 | 77 | 77 | 88 |
| **3e** | *o*-$ClC_6H_4$ | 2.5 | 37 | 37 | 89 |
| **3f** | *p*-$ClC_6H_4$ | 2.5 | 116 | 117 | 89 |
| **3g** | α-Naphthyl | 2.5 | 148-149 | 149-150 | 86 |
| **3h** | β-Naphthyl | 2.0 | 111 | 111 | 88 |
| **3i** | *p*-Anisyl | 2.0 | 91 | 91 | 88 |
| **3j** | 3-Me-4-$ClC_6H_3$ | 2.0 | 95 | 96 | 95 |

a) Yields are of pure isolated products. b) Products were characterized by IR, 1H NMR, physical constants, and by comparison with authentic samples.

## EXPERIMENTAL SECTION

All chemicals were of analytical grade, and solvents were freshly distilled before use. A microwave oven, Kelvinator T-37 model, was used for microwave irradiation with its 100% power. IR spectra were recorded on Bomem MB 104 FTIR spectrometer.

**General Procedure for the Synthesis of Triaryl Phosphates.**- A mixture of sodium hydroxide (3.1 mmol), few drops of water, the phenol (3.1 mmol) and phosphoryl chloride (1 mmol) in a 100 mL beaker was covered with watch glass and exposed to microwaves for 2 to 2.5 min. with heating and cooling at the interval of 30 sec. The reaction was monitored by TLC. After completion of the reaction, the product was extracted with chloroform (3 x 10 mL),[10] and the chloroform layer was washed with 2% sodium hydroxide and water (2 x 25 mL each, respectively). Then the chloroform layer was separated from the aqueous layer, dried over anhydrous $Na_2SO_4$ and evaporated under reduced pressure to give the pure product (checked by TLC using 3 different solvent systems) in excellent yield.

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