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Microwave assisted synthesis of triaryl phosphorothionates

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ABSTRACT

Rapid synthesis of triaryl phosphorothionates were carried out in excellent yields and purity by microwave irradiation, involving nucleophilic displacement reaction between phenoxides and thiophosphoryl chloride.

Key words: Microwave irradiation, water, thiophosphoryl chloride, triaryl phosphorothionates.

INTRODUCTION

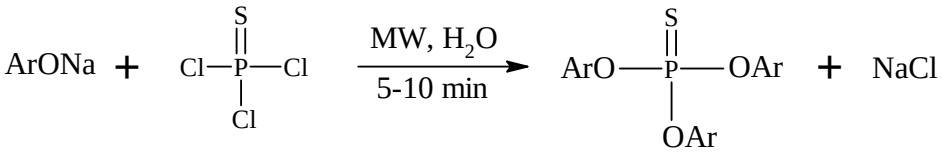
The applications of microwave irradiation in organic synthesis have been reported first by Gedye and Giguere/ Majetich in 1986.[1] Thereafter, more than 4000 articles have been published on the applications of microwave irradiation in organic synthesis called as microwave assisted organic synthesis. A large number of review articles [2] and several books[3] witnessed it, which provides extensive coverage of the applications of microwave irradiation in organic synthesis.

Microwave assisted organic synthesis is one of the emerging technology developed in organic synthesis for chemical research.[2c,4] It has been used for the synthetic chemistry which provides more eco friendly reaction conditions. The main objective of this method is to use as possible as maximum safer raw material efficiently and to reduce chemical waste and reaction time.[5] In organic synthesis and transformations, microwave irradiation became useful technique in a variety of applications.[6] Variety of organic reactions have been carried out by using microwave irradiations.[7] Microwave assisted organic synthesis is energy and time efficient process offering a fast and easy route to organic synthesis.

Triaryl phosphorothionates are important chemicals because of their utility as a thermally stable working fluid for heat pumps,[8] as an effective lubricant, additives, with phenolic and aromatic amines, as antioxidants,[9] and as fire proofing agents.[10] Triaryl phophorothionates are having high thermal stability in lubricant oils, do not decompose even at 423 K for 168 hrs and at 473 K for 72 hrs.[11] In addition triaryl phosphorothionates are also used as functional fluids, containing hydraulic stabilizers.[12]

Several methods were developed for the synthesis of triaryl phosphorothionates.[13-20] These were prepared from thiophosphoryl chloride and three equivalents of phenol in presence of base such as triaryl amine,[21] using Aliquot-336,[17] or by the oxidation of triaryl phosphite with sulfur,[22] and by reacting thiophosphoryl halides with

mixtures of hydroxy aryl compounds and sulfurizing, if necessary.[23] Triaryl phosphorothionates were also prepared by thiophosphoryl chloride with insoluble polymer supported phenoxide ions.[16] However, thiophosphoryl chloride is having low reactivity towards phenol and hence phase transfer catalysts are essential.[17] In view of the importance of triaryl phosphorothionates we report herein a method for rapid synthesis of triaryl phosphorothionates (III) by the reaction of sodium salt of phenoxide ion (I) with thiophophoryl chloride (II) in water under microwave irradiation (Scheme 1).



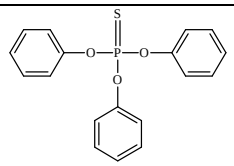
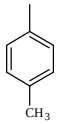
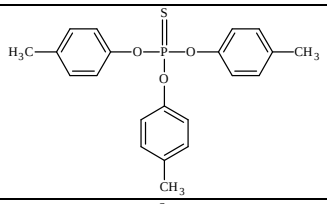
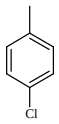
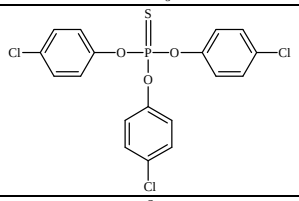
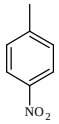
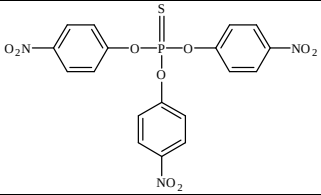
I **II** **III**

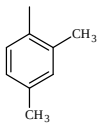
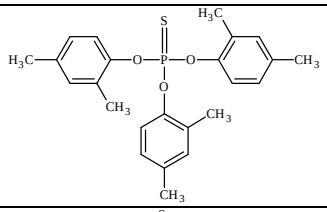
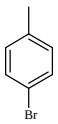
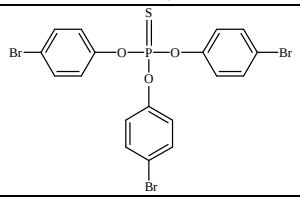
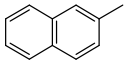
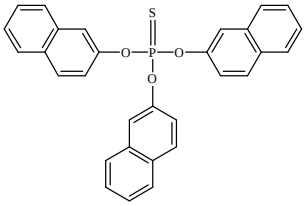
Scheme 1

MATERIALS AND METHODS

An aqueous solution of sodium salt of hydroxyaryl compound (3.1 mmol) and thiophosphoryl chloride (1 mmol) were taken into the 100 ml beaker. It was covered with watch glass and subjected to microwave irradiation (180 W) for 5-10 minutes at the interval of one minute. The reaction was monitored by TLC. After the completion of the reaction, the product was extracted with chloroform (3 x 10 mL) and chloroform layer was washed with 2 % sodium hydroxide (2 x 25 mL). The chloroform layer was then dried over anhydrous sodium sulphate and the solvent was evaporated under reduced pressure to afford triaryl phosphorothionate in essentially pure form.

Table 1 : Synthesis of triaryl phosphorothionates

Sr. No.	Ar	Triaryl Phosphorothionates	Time (min.)	Yield (%)	MP (°C) [Lit] [16]
1			5	91	54 [54]
2			6	89	93 [93-94]
3			7	85	107 [108]
4			10	81	177 [177-179]

5			6	88	63 [63-64]
6			7	85	96 [96-96]
7			8	83	95 [95-96]

RESULTS AND DISCUSSION

Triaryl phosphorothionates were synthesized using non conventional method. Upon exposure to microwave irradiation aqueous solution of sodium salt of hydroxyaryl compound, thiophosphoryl chloride and water afforded the corresponding triaryl phosphorothionates in good to excellent yields. The sodium salt of phenoxide ion with electron donating sunstituents (entries 2, 5) on the aromatic ring underwent faster reaction than that of electron withdrawing sunstituents (entries 3, 4).

CONCLUSION

In conclusion we developed a new method for the rapid synthesis of triaryl phosphorothionates in good to excellent yields by using microwave irradiation. This method is faster, time saving

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