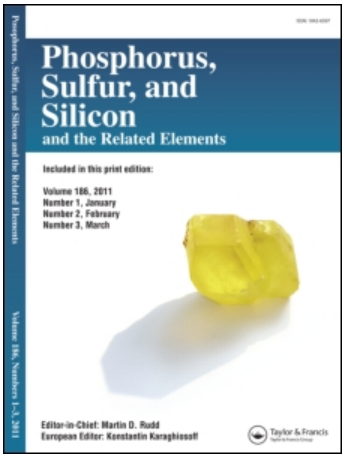

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Microwave Irradiation Technique for Synthesis of Dialkyl Dithiophosphoric Acids

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Online publication date: 27 October 2010

To cite this Article Gümgüm, Bahattin , Bırıcık, Nermin and Baysal, Akın(2002) 'Microwave Irradiation Technique for Synthesis of Dialkyl Dithiophosphoric Acids', Phosphorus, Sulfur, and Silicon and the Related Elements, 177: 10, 2507 — 2512
To link to this Article: DOI: 10.1080/10426500214305
URL: http://dx.doi.org/10.1080/10426500214305

Phosphorus, Sulfur and Silicon, 2002, Vol. 177:2507–2512

1042-6507/02 $12.00 + .00
DOI: 10.1080/10426500290110649

MICROWAVE IRRADIATION TECHNIQUE FOR SYNTHESIS OF DIALKYL DITHIOPHOSPHORIC ACIDS

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(Received November 6, 2001; accepted January 1, 2002)

Microwave heating technique was applied to the preparation of dialkyl dithiophosphoric acids from the reaction of alcohol with phosphorus pentasulphide. A microwave oven (CEM-MDS 2000) was utilized to determine the preparation conditions for the best yield of dialkyl dithiophosphoric acids under atmospheric pressure at various times and power. Six different (C_4–C_9) chain-length of dialkyl dithiophosphoric acids were studied. All experiments were performed in an open Teflon (poly-tetrafluoroethylene) vessel. The results obtained showed that the reaction of dialkyl dithiophosphoric acids can be achieved more rapidly using microwave heating than using conventional procedures.

Keywords: Dialkyl dithiophosphoric acids; microwave irradiation; synthesis

INTRODUCTION

Organophosphorus compounds are important industrial reagents, using alkyl phosphates for extraction of metal ions is well known.[1] When one ore more oxygen atoms of these compounds have been replaced by sulphur atoms, their "soft" thio analogues (organothiophosphorus compounds) have been produced. These compounds have been prepared from the reaction of alcohols with phosphorus pentasulfide,[2–3] or with red phosphorus and sulfur.[4] Various organothiophosphorus compounds were prepared and investigated,[5] and in the last five years a number of reviews were published.[6–10]

The search for a rapid reaction technique has lead several workers to investigate the use of microwave radiation in the chemical reaction

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procedures. The application of microwave dielectric heating techniques for chemical synthesis has attracted considerable interest in recent years, and a wide range of organic and inorganic reactions have been accelerated using microwave heating.[11,12] Application of microwave radiation in organic reactions were started in 1986 with two studies. In the first article, four different types of organic reactions were studied and seven different organic compounds prepared under pressure in a microwave oven.[13] In the second microwave application, Diels-Alder, Claisen and Ene reactions were investigated with a significant decrease in reaction time.[14] Since 1986, the microwave heating technique gradually has gained widespread acceptance as a chemicals-preparation method, and many reviews were published on the synthesis of chemicals or other organic or inorganic reactions by microwave heating.[15–22]

Although microwave irradiation has been commonly used as a thermal energy source in various fields of chemistry,[23–25] there are only a few articles on its applications in organophosphorus compounds,[26–31] and not one on organothiophosphorus compounds.

Newly, phosphonate esters were prepared using a domestic microwave oven, and a comprehensive examination of the Michaelis-Arbuzov reaction under microwave irradiation was reported.[26] In the second new research, several phosphonium salts were prepared using a domestic microwave oven, and the microwave enhanced reaction of triphenylphosphine and an organic halide shows a remarkable rate acceleration under microwave irradiation.[27] In the third article, diethyl alkylphosphonates were efficiently and rapidly prepared from trialkylphosphites and alkyl halides under short microwaves irradiations.[28] In the fourth one, diethyl arylphosphonates were prepared from aryl halides in a commercial microwave oven.[29] The other two articles are related to microwave accelerated Wittig reactions-phosphorus ylides.[30,31]

In the present work, different alcohols (C_4 to C_9) were treated with phosphorus pentasulphide by microwave heating, and the results compared with conventional procedure.[3] Thus in the first case, we have utilized the microwave method at atmospheric pressure for optimization of the preparation of dialkyl dithiophosphoric acids.

EXPERIMENTAL

In this study, a CEM-MDS 2000 model microwave oven was used, with double walled lined vessels made from Teflon-poly(tetrafluoroethylene). The MDS-2000 delivers approximately 630 watts of microwave energy at a frequency of 2450 MHz at full power. The percent power may be

increased in 1% increments and the system is programable to control pressure from 0–200 psi in five separate stages. All of the chemicals used were analytical reagent grade.

Synthesis of Dialkyldithiophosphoric Acids

Dialkyl dithiophosphoric acids were prepared by the reaction of phosphorus pentasulphide with different pure alcohols.

$$4ROH + P_2S_5 \rightarrow 2(RO)_2PSSH + H_2S$$

According to the chemical equation described in the literature[2,3] (0.11 g, $2.5 \cdot 10^{-3}$ mmol) phosphorus pentasulphide was weighed into poly(tetrafluoroethylene) vessels and 0.01 mmol of the investigated alcohols were added. The microwave vessels containing mixture of 0.01 mmol alcohol and $2.5 \cdot 10^{-3}$ mmol phosphorus pentasulphide were placed in microwave oven. Different power stages; 63 W, 315 W, 504 W, and 630 W were applied at various times to determine the optimum conditions for production of dialkyl dithiophosphoric acids. The vessels were allowed to cool to room temperature and excess phosphorus pentasulphide was removed. The acidity of 0.2 g final product was determined by titration of standardised 0.1 M of NaOH solution (Anal. calc. for $(C_7H_{15}O)_2PSSH$: C 51.50, H 9.57, S 19.64, P 9.49, found: C 51.67, H 9.78, S 19.36, P 9.21).

RESULTS AND DISCUSSION

In a conventional synthesis, 4 mmol of anhydrous alcohols were placed in a flask and 1 mmol of phophorus pentasulphide gradually was added with constant stirring under a nitrogen atmosphere for 7–8 h at 72–74°C. The mixture was cooled and excess phophorus pentasulphide removed.[3]

Dialkyl dithiophosphoric acids were prepared by the reaction of phosphorus pentasulphide and alcohols by heating with microwave radiation. The acidity of obtained products were determined by using the titration method with NaOH solution. Preparation conditions of dialkyl dithiophosphoric acids by microwave methods under atmospheric pressure were examined. 63 W, 315 W, 504 W, and 630 W powers were applied to 0.01 mmol of nonyl alcohol and $2.5 \cdot 10^{-5}$ mmol of phosphorus pentasulphide in different times and in a single step to determine appropriate conditions for producing dinonyl dithiophosphoric acid. The power application of 504 W for 3 min was found to be the best condition (Figure 1, Table I). By taking this result into account the preparation

TABLE I The Yield of Dinonyl Dithiophosphoric Acid with Different Microwave Powers and Times

Time (min)	Yield (%) 63 W	315 W	504 W
1	29.90	48.98	62.96
2	49.80	51.48	76.59
3	62.80	67.14	88.90
4	64.00	73.90	79.30
5	84.80	81.50	79.30
6	—	59.90	70.80

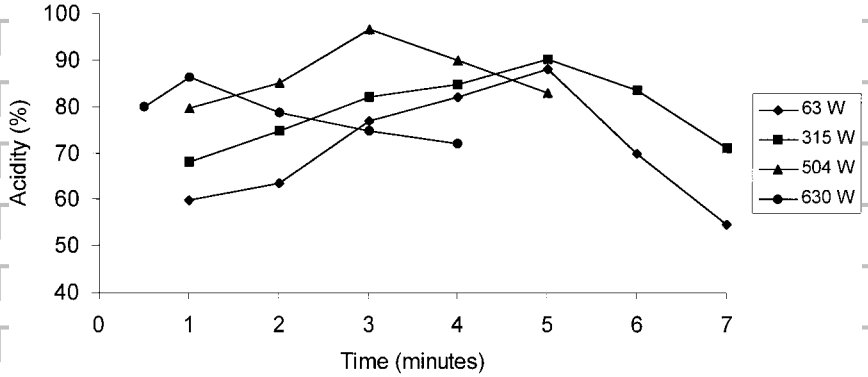

FIGURE 1 The acidity of dinonyl dithiophosphoric acid with different microwave powers.

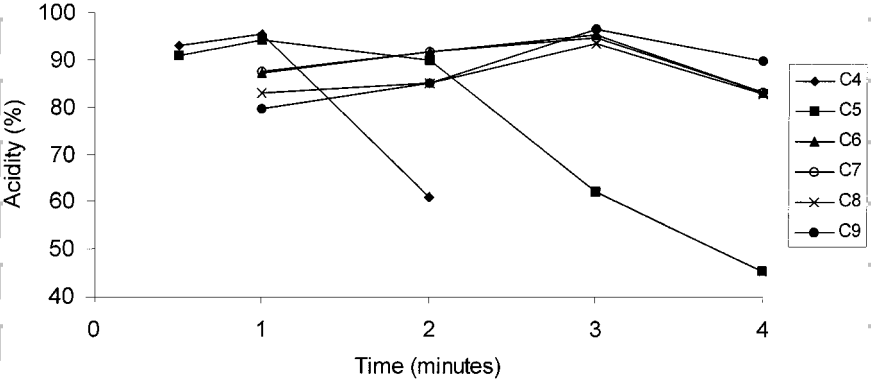

FIGURE 2 Under 504 W fixed power, the acidity of dibutyl, dipentyl, dihexyl, diheptyl, dioctyl, and dinonyl dithiophosphoric acids with different microwave radiation time.

TABLE II Under 504 W Fixed Power for 3 min, the Yields of Dinonyl, Dioctyl, Diheptyl, and Dihexyl, Dithiophosphoric Acids

Compounds	Yield (%)
$(C_9H_{19}OP)_2SSH$	88.9
$(C_8H_{17}OP)_2SSH$	93.7
$(C_7H_{15}OP)_2SSH$	95.3
$(C_6H_{13}OP)_2SSH$	96.6

durations of other dialkyl dithiophosphoric acids were determined under 504 W fixed power (Figure 2, Table II) .

The result shows that excellent yields were obtained within 1–3 min of reaction time at fixed power 504 W. For lower chain alcohols, dibutyl and dipentyl dithiophosphoric acids require less time than that for longer ones, dihexyl, diheptyl, dioctyl, dinonyl dithiophosphoric acids. Similarly, the required reaction time to produce the dialkyl dithiophosphoric acids were decreased by increasing the microwave energy power. It is possible to speculate that there exists a relationship between the chain-length and the reaction time in the microwave radiation, and 1–3 min microwave heating time corresponds to 7–8 h of conventional heating.

In conclusion, we have demonstrated that synthesis of dialkyl dithiophosphoric acid can be accomplished as a new and very rapid method from the reaction of alcohol and phosphorus pentasulphide by microwave radiation.

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