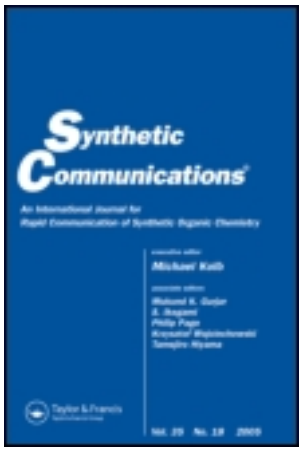

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SURFACE-MEDIATED SOLID PHASE REACTIONS: MICROWAVE ASSISTED ARBUZOV REARRANGEMENT ON THE SOLID SURFACE

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SURFACE-MEDIATED SOLID PHASE REACTIONS: MICROWAVE ASSISTED ARBUZOV REARRANGEMENT ON THE SOLID SURFACE

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ABSTRACT

Microwave assisted Arbuzov rearrangement under solvent-free condition was found to be an efficient method for the preparation of dialkyl alkylphosphonates of alkyl halides. This method is an easy, rapid, and high-yielding reaction for the Arbuzov rearrangement.

Although phosphorus compounds containing the phosphorus–carbon bond are not particularly abundant in nature, their diverse biological activity,[1,2] has for a long time attracted considerable synthetic[3] and pharmacological interest.[4] The Michaelies–Arbuzov rearrangement, also known as the Arbuzov reaction, is a very versatile way to create a phosphorus–carbon bond from a trialkyl phosphite and an alkyl halide.[5] This reaction is one of the most

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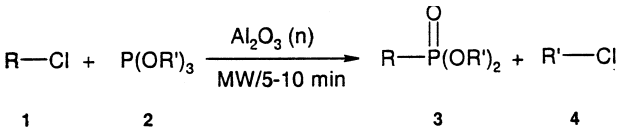
extensively investigated in organophosphorus chemistry and is widely used to prepare phosphonates, phosphinates and phosphine oxides.[6] Basically, the trialkyl phosphites usually used are $(EtO)_3P$, and $(MeO)_3P$. The rearrangement involves the formation of the corresponding alkyl halide (EtX, and MeX) that is volatile in the general experiment conditions of the Arbuzov reaction. There is no doubt that microwave can be used to great effect in organic synthesis; the *in situ* generation of heat is very efficient and can be used to significantly reduce reaction times of numerous synthetically useful organic transformations.[7] To our knowledge, there is no report in the literature on a Michaelies–Arbuzov reaction on the solid surface that assisted by microwave. As a part of our efforts to explore the novel utilities of surface-mediated reaction for the synthesis of organophosphorus compounds,[8–11] we report here a new method for the Arbuzov rearrangement on the solid surface. It is found that alumina (neutral) under solvent-free conditions was capable of producing high yields of dialkyl alkylphosphonates from alkyl chloride and trialkyl phosphite under microwave irradiation (Scheme 1) (Table 1).



Scheme 1.

Table 1. The Arbuzov Reaction for the Preparation of Dialkyl Alkylphosphonates (**3**) Under Solvent-Free Condition Using Microwave Irradiation

Product **3**	R-	R′	Time (min)	Yield[a] (%)
a	$PhCH_2$-	Et-	10	85
b	CCl_3-	Et-	5	78
c	CH_2=CH-CH_2-	Et-	5	73
d	$PhCOCH_2$-CH_2-	Et-	5	90
e	*t*-butyl-	Et-	15	–
f	$PhCH_2$-	Me-	10	80
g	CCl_3-	Me-	5	76
h	CH_2=CH-CH_2-	Me-	5	70
i	$PhCOCH_2$-CH_2-	Me-	5	90
f	*t*-butyl-	Me-	15	–

[a]Isolated Yields.

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As shown in Table 1, benzyl chloride, tetrachloride carbon, allyl chloride, and also 3-chloro-1-phenyl-1-propanone with triethyl phosphite and trimethyl phosphite in the presence of alumina (n), afford the desired products in excellent yields with microwave irradiation. The *t*-butyl chloride is failed in this condition and no Arbuzov rearrangement product was detected.

The other types of alumina (acidic and basic) are not as effective as neutral alumina and usually give relatively low yields of the corresponding products.

Simple work-up, low consumption of solvent, fast reaction rates, mild reaction condition, and good yields of the reaction make this method an attractive and useful contribution to the present methodologies.

EXPERIMENTAL SECTION

General: All chemicals were commercial products and distilled or recrystallized before use. A kitchen type microwave at 2450 MHz (900 W) was used in all experiments. The infrared (IR) spectra were determined neat using a FTIR. ^{1}H NMR (at 60 MHz) spectra were obtained as solutions in deuteriochloroform ($CDCl_3$).

General Procedure for the Preparation of Dialkyl Alkylphosphonates (3) on the Solid Surface

Alumina (Al_2O_3, neutral, 2 g) was added to a mixture of trialkyl phosphite (0.0025 mol) and the alkyl chloride (0.002 mol). This mixture was irradiated by microwave for 5–10 min (Table 1). The reaction mixture was washed with CH_2Cl_2 (200 mL), dried ($CaCl_2$), and the solvent evaporated to give the crude products. Pure product was obtained by distillation under reduced pressure in 73–90% yields.

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