Tetrahedron Letters 49 (2008) 6704–6706

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

N,*N*-Dichloro poly(styrene-co-divinyl benzene) sulfonamide polymeric beads: an efficient and recyclable reagent for the synthesis of dialkyl chlorophosphates from dialkylphosphites at room temperature

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ARTICLE INFO

Article history:
Received 28 July 2008
Revised 7 September 2008
Accepted 10 September 2008
Available online 13 September 2008

Keywords:
Dialkylphosphite
Dialkyl chlorophosphate
Polymer-supported-synthesis

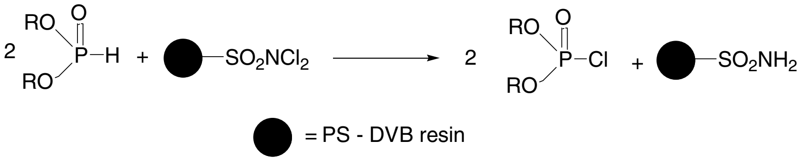
ABSTRACT

An efficient and operationally simple method is developed for the synthesis of dialkyl chlorophosphates from dialkylphosphites using a new chlorine bearing reagent, *N*,*N*-dichloro poly(styrene-co-divinyl benzene) sulfonamide in the form of polymeric beads. The reagent afforded dialkyl chlorophosphates at room temperature, and is recyclable.

Organophosphorus compounds have attracted the attention of researchers because of their wide applications in industrial, agricultural, biochemical, and medicinal areas.[1] Naturally occurring organophosphorus compounds play an important role in the maintenance of life processes.[2–6] It is interesting to note that chemical, physical, and biological properties of organophosphorus compounds are governed by the stereochemical disposition of substituents around the phosphorous atom. One such class of compounds is the dialkyl chlorophosphates. These chlorophosphates are used for the transformation of various functional groups.[7–12] Recently, diethylchlorophosphate has been used as an efficient reagent in cyclization reactions[13] and in regioselective ring opening of epoxides.[14]

Methods described in the literature for the preparation of dialkyl chlorophosphates, involve chlorination of the corresponding phosphites (dialkylphosphites/trialkylphosphites) with reagents such as elemental chlorine,[15] phosgene,[16] SO_2Cl_2,[17] S_2Cl_2,[18] SCl_2,[19] CCl_4,[20] CCl_3NO_2,[21] $PhSO_2NCl_2$,[22] C_2Cl_6,[23] $ClSCCl_3$,[24] $CuCl_2$,[25] perchlorofulvalene,[26] and *N*-chlorosuccinimide.[27] Among these procedures, only a few can be considered as convenient laboratory methods for the synthesis of dialkyl chlorophosphates. Most of these reported methods either use reagents or produce undesired by-products, which are difficult to remove from the sensitive chlorophosphates,[15–20] while others are time consuming, involve expensive and unstable reagents, and require harsh conditions. A modified method (the so-called Atherton–Todd method) makes use of CCl_4 and a tertiary base to generate dialkyl chlorophosphates in situ, but it has limited scope in the formation of P–N compounds.[8d] Our aim in this research work was to overcome the limitations and drawbacks of the reported methods.

In recent years, the use of recyclable reagents has received considerable interest in organic synthesis. This prompted us to explore



Scheme 1. Dialkyl chlorophosphates prepared from dialkylphosphites using the polystyrene divinylbenzene (PS-DVB) bound reagent.

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doi:10.1016/j.tetlet.2008.09.044

Table 1

Isolated yields of dialkyl chlorophosphates from the reaction of dialkylphosphites and *N,N*-dichloro poly(styrene-co-divinyl benzene) sulfonamide polymeric beads[a]

Entry (°C/(mm/Hg))	R	^{31}P NMR (ppm)	Time (h)	Yield (%)	B.P (°C/(mm/Hg))
1	CH_3	6.34	2.00	95	75–77/20
2	C_2H_3	5.04	2.00	96	85–87/10
3	C_3H_7	5.48	2.30	97	102–103/10
4	*i*-C_3H_7	3.76	2.30	96	90–92/10
5	C_4H_9	4.58	2.30	94	115–117/10
6	*i*-C_4H_9	4.16	2.30	95	122–124/10
7	*sec*-C_4H_9	4.71	2.30	92	140–142/5
8	C_5H_{11}	4.59	3.00	94	131–132/1
9	*i*-C_5H_{11}	3.58	3.00	96	122–124/1
10	C_6H_{13}	4.25	3.15	98	Undistilled
11	$C_6H_5CH_2$	4.7	3.15	94	Undistilled
12	C_6H_5	6.2	3.45	93	140–142/1

[a] All products gave satisfactory NMR and GC–MS data and compared well with authentic samples. ^{31}P NMR spectra were recorded in $CDCl_3$ at 162 MHz.

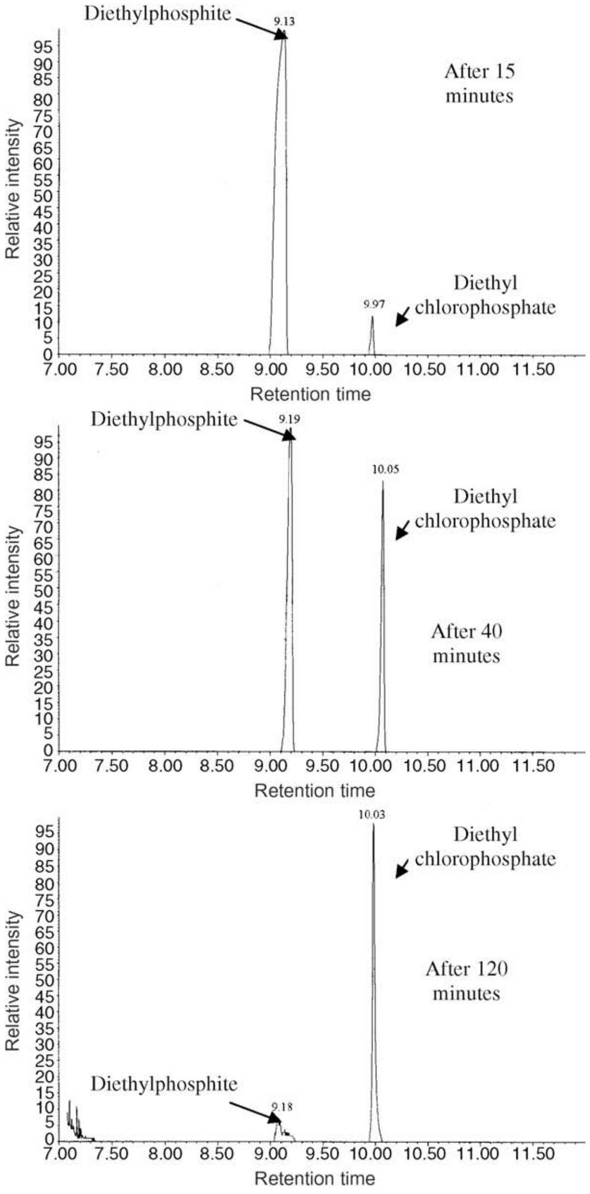

Figure 1. Progress of a typical reaction as monitored by GC–MS analysis at different time intervals.

the possibility of using the stable, nontoxic, recyclable, and efficient positive chlorine releasing reagent, *N,N*-dichloro poly(styrene-co-divinyl benzene) sulfonamide polymeric beads.[28] It has been incorporated as a reactive ingredient in a formulation developed in our laboratory to decontaminate bis(2-chloroethyl) sulfide (sulfur mustard), a chemical warfare agent.[29] Having established a commercially synthetic procedure for *N,N*-dichloro poly(styrene-co-divinyl benzene) sulfonamide polymeric beads, we investigated its use as an alternative reagent for the conversion of dialkylphosphites to dialkyl chlorophosphates and report our results herein.

This development enables us to obtain almost all quantitative yields of products in short reaction times. The room temperature (20–25 °C) reaction of various dialkylphosphites with *N,N*-dichloro poly(styrene-co-divinyl benzene) sulfonamide polymeric beads afforded the corresponding dialkyl chlorophosphates in 3–4 h in excellent yields (Scheme 1, Table 1).

The important aspect of this method is its simplicity. *N,N*-Dichloro poly(styrene-co-divinyl benzene) sulfonamide polymeric beads were suspended in a suitable solvent, for example, acetonitrile. To this suspension, the dialkylphosphite (an equivalent amount to the active chlorine available on the PS-DVS beads) was added, and the mixture was stirred gently using a magnetic stirrer.[30] The reaction was monitored by removing an aliquot and analyzing by GC–MS. The progress of a typical reaction as monitored by GC–MS is depicted in Figure 1.

When all the dialkylphosphite had been consumed, the reaction was decanted, and the beads were washed with solvent. After removing the solvent by distillation, the products were obtained in pure form by vacuum distillation. The yields and boiling points of the products are summarized in Table 1. The PS-DVB beads were recovered and re-chlorinated using the reported method.[29] These beads could be reused for the preparation of dialkylchlorophosphates. Thus, the advantages of this method are room temperature reactions, simple workups, and recyclability of the reagent. We found that both alkyl and aryl phosphates reacted efficiently at room temperature to produce the corresponding chlorophosphates in excellent yields. Aliphatic dialkylphosphites reacted a little more rapidly compared to aromatic phosphites (entries 1–11 vs 12, Table 1).

In conclusion, we have described an efficient reagent for the rapid and convenient conversion of dialkylphosphites to dialkyl chlorophosphates under mild conditions using *N,N*-dichloro poly(styrene-co-divinyl benzene) sulfonamide polymeric beads, as a stable and non-toxic reagent at room temperature.

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