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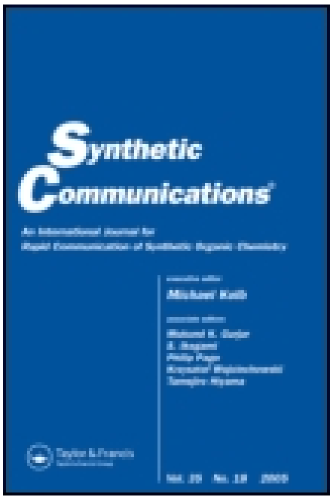

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PREPARATION OF ACYL PHOSPHATES ON THE SURFACE OF MAGNESIA

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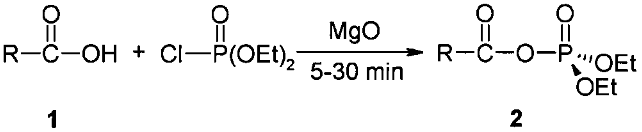
ABSTRACT

Phosphorylation of carboxylic acids with diethyl chlorophosphate on the surface of magnesia is an easy, rapid, safe and good yielding reaction.

Organophosphorus compounds have found a wide range of application in the areas of industrial, agricultural, and medicinal chemistry owing to their biological and physical properties as well as their utility as synthetic intermediates.[1] The synthesis of phosphate esters is an important objective in organic synthesis, since they have found use in the preparation of biological active molecules, and also versatile intermediate in synthesis of amides and esters.[2,3] Owing to their synthetic and biological values, the chemistry of phosphates has stimulated an increasing interest and the development of new methodologies for their preparation still remains of great interest.[4]

Surface-mediated solid phase reactions are of growing interest[5] because of their ease of set up and work-up, mild reaction conditions, rate of the reaction, selectivity, high yields, lack of solvent and the low cost of the reactions in comparison with their homogeneous counterparts. As a part of our efforts to explore the utility of surface-mediated reactions, for synthesis of organophosphorus compounds,[6–10] herein I wish to report a new method for the preparation of acyl phosphates by reaction of carboxylic acids on the solid surface. It is found magnesia under solvent-free conditions was capable of producing high yields of acyl phosphates from phosphorylation of carboxylic acids with diethyl chlorophosphate under mild reaction conditions (Scheme 1 and Table 1).



Scheme 1.

As shown in Table 1, *o*-, *m*- and *p*-substituted benzoic acid afforded the desired products in excellent yields (**2a–2h**). The reaction also proceeded in high yields for naphthalene carboxylic acid in the presence of magnesia (**2i**). Aliphatic carboxylic acids gave desired products in good yields. The reaction also proceeded in high yields for 1-hydroxyfurfuryl, α-naphthyl, and β-naphthyl phosphonates (**2p–r**).

The reactions are clean with no tar formation, and interestingly, no cleavage of the C–O–P bond is observed. Indeed a wide range of carboxylic acids was converted to corresponding acyl phosphates under this condition.

Table 1. The Preparation of Acyl Phosphates (**2**) Under Solvent-Free Condition

Product **2**	R-	Time (min)	Yield[a] (%)
a	Ph-	5	90
b	*p*-$CH_3C_6H_4$-	20	85
c	*p*-ClC_6H_4-	5	85
d	*p*-FC_6H_4-	10	90
e	*p*-$O_2NC_6H_4$-	5	90
f	*m*-$CH_3C_6H_4$-	30	80
g	*m*-ClC_6H_4-	5	90
h	*o*-ClC_6H_4-	5	90
i	α-Naphthyl	25	85
j	CH_3-	30	76
k	$PhCH_2$-	15	80

[a]Isolated yields.

Acidic, neutral, and basic alumina is not as effective as magnesia and usually give low yields of the corresponding esters.

In summary, simple work-up, low consumption of solvent, relatively fast reaction rates, mild reaction condition, good yields, and selectivity of the reaction make this method an attractive and a useful contribution to 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. The infrared (IR) spectra were determined neat using a FTIR. ^{1}H NMR (at 90 MHz) spectra were obtained as solutions in deuteriochloroform ($CDCl_3$).

General Procedure for Phosphorylation of Carboxylic Acids with Diethyl Chlorophosphonate on the Surface of Magnesia

This solvent-free method is operationally simple. Magnesia (0.3 g) was added to a mixture of diethyl chlorophosphate (0.86 ml, 0.006 mol) and the carboxylic acid (0.005 mol). This mixture was stirred at room temperature for 5–30 min (Table 1). The solid mixture was washed with dichloromethane (4 × 25). The solution was then washed with saturated $NaHCO_3$ solution and saturated sodium chloride solution and dried over $MgSO_4$. After evaporating of solvent, the crude product was isolated in a pure state by distillation under vacuum in 76–90% yield.

Acyl phosphates 2: All products gave satisfactory spectral data in accord with the assigned structures. [e.g. for **2a** ^{1}H NMR ($CDCl_3$, TMS) δ: 1.22 (t, 3H, $J = 6$ Hz, $-OCH_2CH_3$), 1.28 (t, 3H, $J = 6$ Hz, $-OCH_2CH_3$), 4.05–4.72 (m, 4H, $-OCH_2CH_3$), 7.20 (t, 2H, $J = 7.3$ Hz), 7.44 (t, 1H, $J = 7.3$ Hz), 8.18 (d, 2H, $J = 7.3$ Hz); IR (neat): ν 1795, 1735 (C=O), 1590 (Ar), 1242 (P=O), 1103–978 (P-O-Et) cm^{-1}].

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