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Surface-mediated solid-phase reactions: the preparation of acyl phosphonates by oxidation of 1-hydroxyphosphonates on the solid surface

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Abstract

Alumina-supported CrO_3 , under solvent-free conditions, was found to be an efficient oxidizing reagent for the preparation of acyl phosphonates from 1-hydroxyphosphonates. This method is an easy, rapid, and high-yielding reaction for the preparation of acyl phosphonates from 1-hydroxyphosphonates. © 2000 Elsevier Science Ltd. All rights reserved.

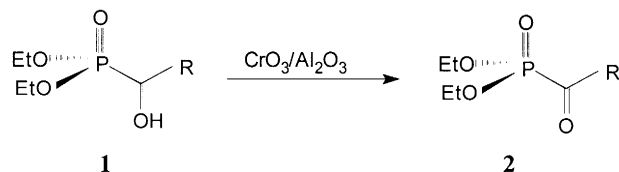
Keywords: Arbuzov reactions; oxidation; 1-hydroxyphosphonates; acyl phosphonates.

Acyl phosphonates have a number of properties that make them attractive as reagents or intermediates for synthesis. These properties have stimulated a recent resurgence of interest in the chemistry of such compounds.^{1–6} For several years it has been known that the carbonyl of an acyl phosphonate is activated towards attack by nucleophiles and that the carbon–phosphorus bond is readily cleaved.⁷ This property makes acyl phosphonates potentially useful acylating agents, but also susceptible to hydrolysis and difficult to handle.⁷ Acyl phosphonates are usually prepared by a Michaelis–Arbuzov reaction between a trialkyl phosphite and acid chloride.⁸ The Michaelis–Arbuzov reaction works well for the less complex aroyl and alkanoyl chlorides where purification by distillation is possible. However, there has been less success in the preparation of α,β -unsaturated acyl phosphonates where multiple addition products are often observed,^{9a,b} and the products are thermally or acid-sensitive compounds.^{9c} An alternative method for the preparation of acyl phosphonates is the oxidation of the corresponding hydroxyphosphonate.¹⁰ Although there have been sporadic reports on the oxidation of hydroxyphosphoryl compounds, the reactions developed tend to work well with isolated examples, but are not usually general for a range of substrates.

Surface-mediated solid phase reactions are of growing interest¹¹ 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 part of our efforts to

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explore the utility of surface-mediated reactions,^{12–14} in this report a new method for the preparation of acyl phosphonates by oxidation of 1-hydroxyphosphonates on the solid surface is described. It is found that alumina (neutral)-supported CrO₃ under solvent-free conditions was capable of producing high yields of acyl phosphonates from 1-hydroxyphosphonates under mild reaction conditions (Scheme 1, Table 1).



Scheme 1.

Table 1
Preparation of acyl phosphonates (2) by solvent-free oxidation of 1-hydroxyphosphonates

Product 2	R-	Time (hr)	Yield ^a (%)	Product 2	R-	Time (hr)	Yield ^a (%)
a	C ₆ H ₅ -	4	89	j	Furfuryl	3	75
b	<i>p</i> -CH ₃ C ₆ H ₄ -	6	85	k	α -naphthyl	8	86
c	<i>p</i> -ClC ₆ H ₄ -	4	90	l	β -naphthyl	4	85
d	<i>p</i> -O ₂ NC ₆ H ₄ -	2.5	85	m	Ph-CH=CH-	6	65
e	<i>p</i> -CH ₃ OC ₆ H ₄ -	8	78	n	Me-CH=CH-	6	70
f	<i>o</i> -ClC ₆ H ₄ -	6	75	o	Ph-CHCH ₃	12	75
g	<i>o</i> -O ₂ NC ₆ H ₄ -	4	70	p	PhCH ₂ CH ₂ -	10	80
h	<i>m</i> -O ₂ NC ₆ H ₄ -	3	85	q	<i>n</i> -C ₄ H ₉ -	10	75
i	2, 4-Cl ₂ C ₆ H ₃ -	8	80	r	<i>n</i> -C ₃ H ₁₁ -	10	78

a. Isolated Yield.

As shown in Table 1, *o*-, *m*- and *p*-substituted 1-hydroxyphosphonates, in the presence of alumina supported chromium(VI) oxide, afforded the desired products in excellent yields (**2a–i**). The reaction also proceeded in high yields for 1-hydroxyfurfuryl, α -naphthyl, and β -naphthyl phosphonates (**2j–l**). 1-Hydroxyalkyl and α,β -unsaturated phosphonates also afforded the acyl phosphonates in excellent yields (**2m–2r**).

The reactions were relatively clean with no tar formation, and interestingly, no cleavage of the C–P bond was observed. Indeed, a wide range of 1-hydroxyphosphonates were converted to corresponding acyl phosphonates under this condition.

This solvent-free oxidation method is operationally simple. Thirty mmol of the reagent is prepared by the combination of CrO₃ (30 mmol, 3 gr, finely ground) and alumina (Al₂O₃, neutral, 5.75 g) in a mortar and pestle by grinding them together until a fine, homogeneous, orange powder is obtained (5–10 min). The 1-hydroxyphosphonate¹⁵ (10 mmol) is added to this reagent. After 2.5–12 h (Table 1) of vigorous stirring, the reaction mixture is washed with CH₂Cl₂ (200 mL), dried (Na₂SO₄), and the solvent evaporated to give the crude products. Pure product¹⁶ is obtained by distillation under reduced pressure in 65–90% yields.

In summary, a 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 useful contribution to present methodologies.

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- Procedure for the preparation of 1-hydroxyphosphonates (**1**): Magnesium oxide (2 g) was added to a stirred mixture of diethyl phosphite (0.02 mol) and aldehyde (0.02 mol) at room temperature. After 2 h the mixture was washed by dichloromethane (4×50 mL) and dried with CaCl₂; evaporation of the solvent gave the crude product. The products were crystallized from CH₂Cl₂:*n*-hexane (1:2) or distilled under reduced pressure.
- All products gave satisfactory spectral data in accord with the assigned structures and literature reports⁸ (e.g., for **2a** δ_H (CDCl₃, TMS): 1.15–1.30 (2t, 6H, J=6 Hz, 2-OCH₂CH₃), 4.05–4.7 (2q, 4H, J=6 Hz, 2-OCH₂CH₃), 7.13–8.1 (m, 5H); IR (neat): ν 1659 (C=O), 1610 (Ar), 1258 (P=O), 1103–1025, 978 (P–O–Et) cm⁻¹].