Convenient Synthesis of Unesterified Acylphosphonic Acids

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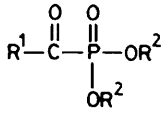
Summary A general method for the synthesis of a new type of compounds, unesterified acylphosphonic acids, is described, involving reactions of tris(trimethylsilyl) phosphite with acyl chlorides followed by solvolysis of the products using aniline-containing alcohols.

REACTIONS of trialkyl phosphites with acyl halides giving dialkyl acylphosphonates (**1a**) are well known.[1] However, it has not been possible so far to convert esters of acylphosphonic acids into the corresponding unesterified acids (**1b**) except in the case of diethyl ethoxycarbonylphos-

phonate (**1c**) reported by Warren.[2] This is because acid or alkaline treatment of (**1a**) usually leads to cleavage of the P–C bond prior to hydrolysis of the ester-linkages.



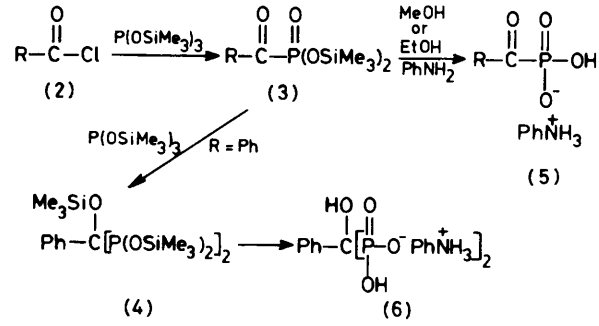
(1)

	R^1	R^2
a;	Alkyl or Aryl	Alkyl or Aryl
b;	Alkyl or Aryl	H
c;	OEt	Et

Orlov and his co-workers[3] reported the reaction of tris-(triethylsilyl) phosphite with some acyl chlorides to give bis(triethylsilyl) esters of acylphosphonic acids. We also know[4] that trimethylsilyl groups of the silyl esters of phosphonic and phosphoric acids can be removed simply by addition of water or alcohols. Therefore, it should be possible to prepare unesterified acylphosphonic acids by solvolysis of the trimethylsilyl esters of acylphosphonic acids obtained by the reaction of acyl chlorides with tris-(trimethylsilyl) phosphite which is more readily available than $P(OSiEt_3)_3$. For example, when $P(OSiMe_3)_3$ was allowed to react with 1 equiv. of benzoyl chloride (**2**; R = Ph) in dry benzene at room temperature for 3 h, bis(trimethylsilyl) benzoylphosphonate (**3**; R = Ph) was obtained in 72% yield. Other acylphosphonate derivatives of (**3**) were similarly obtained (Table).†

1-trimethylsilyloxybenzylphosphonic acid (**4**) was obtained in 76% yield as the major product.

Free acylphosphonic acids can be obtained either by treatment of (**3**) with ethanol or by exposing (**3**) to air for several hours. However, the products from the former



reaction failed to crystallise and those from the latter were contaminated with traces of inorganic phosphorus oxyacids Therefore, the unesterified acylphosphonic acids were isolated as the monoanilinium salts (**5**). Thus, a number of compounds (**3**) were successfully converted into crystalline monoanilinium salts of the corresponding unesterified acylphosphonic acids (**5**) in 89—99% yields by addition of aniline-containing methanol or ethanol, except for (**5**; R = Me or Et) which were isolated as the barium salts (see Table). Similarly, the anilinium salt of the bisphosphonic

TABLE. Reactions of tris(trimethylsilyl) phosphite with acyl chlorides.[a]

RCOCl (**2**) R	Compound (**3**) Yield/%	Reaction time/h	B.p./°C) (mmHg)	Compound (**5**) Yield/%	M.p./°C
Ph	72	2	140—145(3·0)	93	172(decomp.)
C_6H_4Cl-*p*	77	2	137—140(0·25)	94	206—207 (decomp.)
C_6H_4OMe-*p*	72	2	197—199(10)	99	183 (decomp.)
Me	50	2	75—76(0·6)	89	>200[b]
Et	63	2	103—106(0·5)	92	>200[b]
OEt	92	5	95—96(0·45)	98	163 (decomp.)
OCH_2CCl_3	91	2	124—127(0·6)	96	163 (decomp.)

[a] Reactions were carried out in dry pyridine. For the preparation of (**5**) 2 equiv. of aniline in alcohol was used. [b] Obtained as the barium salt.

These reactions usually give rise to carbonyl adducts formed as a result of the successive addition of $P(OSiMe_3)_3$ to (**3**). Thus, when 2 equiv. of $P(OSiMe_3)_3$ was employed in the above reaction, tetrakis(trimethylsilyl) ester of acid (**6**),[5] m.p. 226—227 °C, was successfully obtained in 93% yield.

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† All new compounds gave satisfactory elemental analyses.

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