

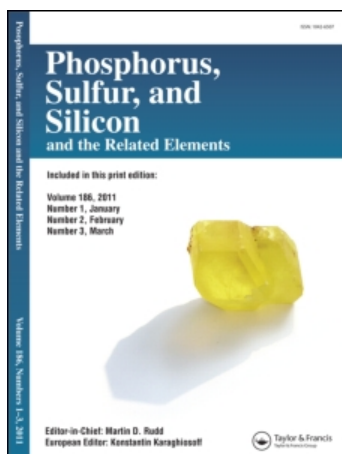
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A NOVEL SYNTHESIS OF DIALKYL 1-TRIMETHYLSILOXY ALLYL PHOSPHONATES

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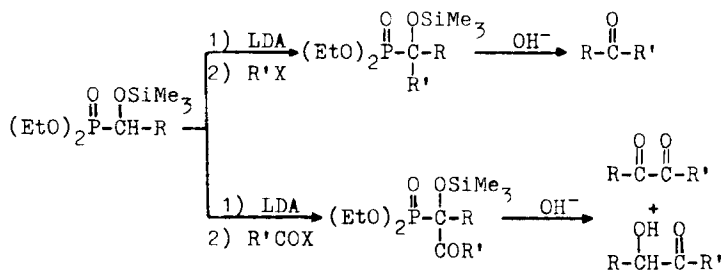
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Dialkyl 1-trimethylsilyloxy allylphosphonates (**3a–3f**) were synthesized by a one-pot reaction of trialkyl phosphite (**1**), carbonyl compounds (**2**) and trimethylchlorosilane. The procedure was carried out under very mild conditions and was very easy to conduct. The structures of (**3**) were confirmed by IR, ¹HNMR, ³¹P NMR and MS.

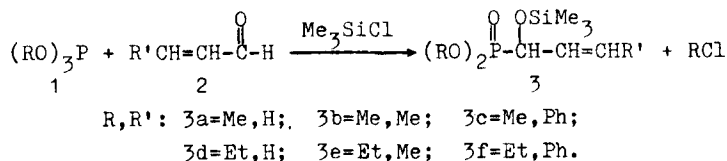
Key words: Phosphite, trimethylchlorosilane, trimethyl silyloxy phosphonate, carbonyl compound.

INTRODUCTION

1-Trimethylsilyloxy phosphonates, compounds containing both phosphorus and silicon atoms, have obvious physiological activities and potential medical functions.¹ They are also widely used as a starting material or intermediates in organic synthesis.² T. Hata, for example, has reported that 1-trimethylsilyloxy alkyl phosphonates are successfully used as novel anion equivalents undergoing facile alkylation or acylation with various halogen compounds to afford the corresponding acylated products in good yields.^{3,4}



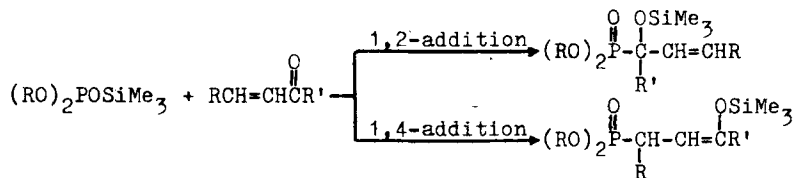
1-Trimethylsilyloxy phosphonates are usually synthesized by the reaction between silyl phosphites containing a P—O—Si bond and carbonyl substrates.^{5,6} First to prepare a very unstable silyl phosphite must be involved and the reaction carried out under an inert atmosphere with the exclusion of oxygen and moisture.⁷ In this paper, we adopted a method to synthesize dialkyl 1-trimethylsilyloxy allyl phosphonate (**3**) by a one-pot reaction of trialkyl phosphite (**1**), unsaturated aldehyde (**2**), and trimethylchlorosilane. Six title compounds (**3a–3f**) were synthesized in this way, their structures were verified by means of Infrared spectrum, Nuclear Magnetic Resonance spectrum, and Mass spectrum.



DISCUSSION

The reaction takes place by mixing the three reactants in equimolar proportions generally with or without solvent, by decrease or increase of the temperature and allowing the resulting mixture to stand until formation of the desired organosilicon phosphorus compound is completed. In practice, (1) and trimethylchlorosilane may be first mixed together and then (2) added to the resulting mixture, or (1) and (2) be mixed and then trimethylchlorosilane added thereto. In most instances, the three reactants can be mixed gradually at a low temperature. Completion of the reaction may be assured by heating the resulting mixture to a temperature from 50°C to 80°C. The reaction may be carried out smoothly even under atmospheric conditions. Removing the by-product and volatile material, the dialkyl 1-trimethylsilyloxy allyl phosphonates are obtained by vacuum distillation or rectification of the residue in a packed column.

This reaction, in which only carbonyl addition products were obtained, is different from the reaction of silyl phosphite and unsaturated carbonyl compounds in that the latter provided both carbonyl 1,2-addition and conjugative 1,4-addition products.^{5,8}



The dominant 1,2-addition taking place in this reaction is owed to the low electron density and little steric hindrance at the carbonyl carbon atom in unsaturated aldehydes. However, a nucleophilic addition predominantly to C=O (1,2-addition) or to β -C (1,4-addition) depends not only on the unsaturated aldehydes, but also on phosphite esters. (RO)₃P has nucleophilic reactivity showing only 1,2-addition to carbonyl group and unable to produce a 1,4-addition to β -C. Yet (RO)₂POSiMe₃ is active enough to react with both C=O and β -C, so it is indiscriminating in the reaction and both additions take place.

The difference between reactions is well explained by the principle of hard and soft acid and base (SHAB).⁹ Here the phosphite esters acted as bases and carbonyl substrates as acids. The SHAB principle states that hard acids react preferentially (both kinetically and thermodynamically) with hard bases, and soft with soft. The words acid and base here can be replaced by electrophile and nucleophile. Thus (RO)₃P, harder nucleophiles than (RO)₂POSiMe₃, prefer to react with the hard electrophile C=O (1,2-addition) rather than react with the soft β -C (1,4-addition).

EXPERIMENTAL

Trialkyl phosphite (1) was prepared as described in Reference 10. All materials used were freshly distilled. IR data were recorded on a Perkin-Elmer Model 983 spectrophotometer; NMR spectra were

measured on Varian Associates Model XL-200 spectrometer, chemical shifts were reported in ppm on the scale relative to TMS internal standard in CDCl_3 for ^1H or 85% H_3PO_4 external standard for ^{31}P ; MS were obtained with a Hitachi GC-MS-80A spectrometer.

Dimethyl 1-trimethylsilyloxy 2-propenyl phosphonate (3a): 5.6 g (45 mmol) trimethyl phosphite and 2.5 g (45 mmol) acrolein mixed in flask under ice-bath, 4.8 g (45 mmol) trimethylchlorosilane was added with stirring, then the ice-bath was removed and the flask heated gradually to 50°C for 3 hours, the low boiler was distilled out and the residual material was distilled under reduced pressure to give 8.4 g (80% of theory) of transparent liquid of **3a**. b.p. $70\text{--}73^\circ\text{C}$ (2 mm). IR: 1630 ($\text{C}=\text{C}$), 1245 ($\text{P}=\text{O}$), 1050, 1030 ($\text{P}-\text{O}-\text{C}$, $\text{Si}-\text{O}$); ^1H NMR: 6.2–5.7 (m, 1H, vinyl H), 5.5–5.0 (m, 2H, vinyl H), 4.3 (d, 1H, PCHOSi), 3.8 (d, 6H, 2OCH_3), 0.2 (s, 9H, 3SiCH_3); ^{31}P NMR: 18.2; MS: 238 (M^+).

Dimethyl 1-trimethylsilyloxy 2-butenyl phosphonate (3b): 5.6 g (45 mmol) trimethyl phosphite, 3.2 g (45 mmol) crotonaldehyde, and 4.8 g (45 mmol) trimethylchlorosilane reacted at 50°C for 3.5 h to give a colorless liquid of **3b** 8.8 g (78%). bp. $93\text{--}95^\circ\text{C}$ (2mm). IR: 1658 ($\text{C}=\text{C}$), 1255 ($\text{P}=\text{O}$), 1040 ($\text{P}-\text{O}-\text{C}$, $\text{Si}-\text{O}$); ^1H NMR: 6.0–5.5 (m, 2H, vinyl H), 4.6 (d, 1H, PCHOSi), 4.0 (d, 6H, 2OCH_3), 1.7 (d, 3H, CH_3), 0.2 (s, 9H, 3SiCH_3); ^{31}P NMR: 20.3.

Dimethyl 1-trimethylsilyloxy 3-phenyl 2-propenyl phosphonate (3c): 5.6 g (45 mmol) trimethyl phosphite, 5.8 g (45 mmol) cinnamic aldehyde and 4.8 g (45 mmol) trimethylchlorosilane at 80°C reacted for 2.5 h to give a light yellow liquid of **3c**, 10.2 g (73%). IR: 1670 ($\text{C}=\text{C}$), 1600 (aromatic ring), 1250 ($\text{P}=\text{O}$), 1055, 1030 ($\text{P}-\text{O}-\text{C}$, $\text{Si}-\text{O}$); ^1H NMR: 7.5–7.2 (m, 5H, C_6H_5), 6.7–6.5 (m, 2H, vinyl H), 4.6 (d, 1H, PCHOSi), 4.2 (d, 6H, 2OCH_3), 0.1 (s, 9H, 3SiCH_3); ^{31}P NMR: 19.8.

Diethyl 1-trimethylsilyloxy 2-propenyl phosphonate (3d): a colorless liquid (76%), bp. $101\text{--}103^\circ\text{C}$ (3mm). IR: 1635 ($\text{C}=\text{C}$), 1252 ($\text{P}=\text{O}$), 1050, 1030 ($\text{P}-\text{O}-\text{C}$, $\text{Si}-\text{O}$); ^1H NMR: 6.0 (m, 1H, vinyl H), 5.5–5.2 (m, 2H, vinyl H), 4.5 (d, 1H, PCHOSi), 4.2 (m, 4H, 2OCH_2), 1.7 (d, 3H, CH_3), 1.2 (t, 6H, 2CH_3), 0.2 (s, 9H, 3SiCH_3); ^{31}P NMR: 18.7; MS: 266 (M^+).

Diethyl 1-trimethylsilyloxy 2-butenyl phosphonate (3e): a colorless liquid (74%), bp. $120\text{--}122^\circ\text{C}$ (3mm). IR: 1670 ($\text{C}=\text{C}$), 1250 ($\text{P}=\text{O}$), 1050, 1030 ($\text{P}-\text{O}-\text{C}$, $\text{Si}-\text{O}$); ^1H NMR: 6.0–5.5 (m, 2H, vinyl H), 4.5 (d, 1H, PCHOSi), 4.1 (m, 4H, 2OCH_2), 1.7 (d, 3H, CH_3), 1.2 (t, 6H, 2CH_3), 0.2 (s, 9H, 3SiCH_3); ^{31}P NMR: 19.5.

Diethyl 1-trimethylsilyloxy 3-phenyl 2-propenyl phosphonate (3f): a light yellow liquid (70.5%), bp. $165\text{--}168^\circ\text{C}$ (3 mm). IR: 1674 ($\text{C}=\text{C}$), 1600 (aromatic ring), 1250 ($\text{P}=\text{O}$), 1060, 1027 ($\text{P}-\text{O}-\text{C}$, $\text{Si}-\text{O}$); ^1H NMR: 7.5–7.2 (m, 5H, C_6H_5), 6.7–6.3 (m, 2H, vinyl H), 4.7 (d, 1H, PCHOSi), 4.1 (m, 4H, 2OCH_2), 1.3 (t, 6H, 2CH_3), 0.1 (s, 9H, 3SiCH_3); ^{31}P NMR: 19.2; MS: 342 (M^+).

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