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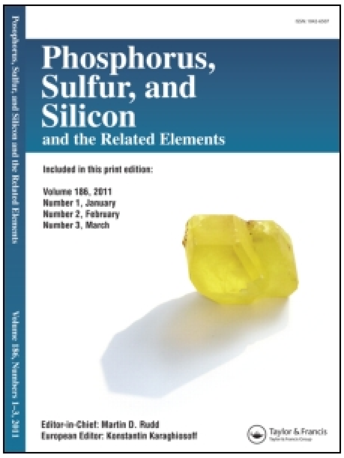

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SYNTHESIS OF DIETHYL 1-(TRIMETHYLSILYL)-2-PROPENYLPHOSPHONATE

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SYNTHESIS OF DIETHYL 1-(TRIMETHYLSILYL)-2-PROPENYLPHOSPHONATE

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Synthesis of 1-(trimethylsilyl)-2-propenylphosphonic diethyl ester **5** from allylic alcohol and diethylchlorophosphite in the presence of triethylamine by [2,3]-sigmatropic rearrangement of the prepared allyldiethylphosphite **2** with formation of the diethyl 2-propenylphosphonate **3** and following reaction of its carbanion **4** with trimethylchlorosilane is described.

Keywords: allyldiethylphosphite; [2,3]-sigmatropic rearrangement; diethyl 2-propenylphosphonate; diethyl 1-(trimethylsilyl)-2-propenylphosphonate

INTRODUCTION

The literature on the chemistry of allylic compounds has been reviewed. [1] Allyl and vinyl phosphorus compounds are part of the subject of a comprehensive treatment of organophosphorus monomers and polymers [2] and much of their chemistry is treated explicity or is implied in the numerous preparative procedures given. Although the preparation [3, 4] of 2-alkenylphosphonates and their synthetic applications [5, 6] have been well studied, the synthesis of dialkyl esters of 2-propenylphosphonic acid [7] and their utilization [6] have been little reported.

The reactions of lithiated esters of 2-alkenylphosphonic acids with carbon electrophiles have been investigated. [8] Diethyl 2-propenylphosphonate was first chosen as a model substrate and its reactions with carbonyl compounds were studied. The reaction with aldehydes [9] led to the formation of α-adducts as kinetic, and of γ-adducts as thermodynamic products. The former products could either isomerize to γ-adducts *via* the reversal of the condensation step, or undergo fragmentation to the corresponding diene. The reaction with α,β-unsaturated ketones and carboxylic esters were also studied, [10] and were found to proceed by three types of reactions: i) simple nucleophilic addition; ii) addition-elimination; iii) multiple addition. On the other hand, the reaction of lithiated diethyl 3-methyl-2-butenylphosphonate and trimethylchlorosilane has been reported [11] to yield the corresponding phosphorylated and silylated 2-butene.

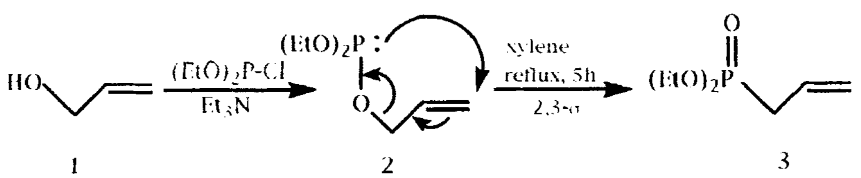
We now describe a simple method for the preparation of 2-propenylphosphonate by [2,3]-sigmatropic rearrangement and its application to the construction of diethyl 1-(trimethylsilyl)-2-propenylphosphonate.

RESULTS AND DISCUSSION

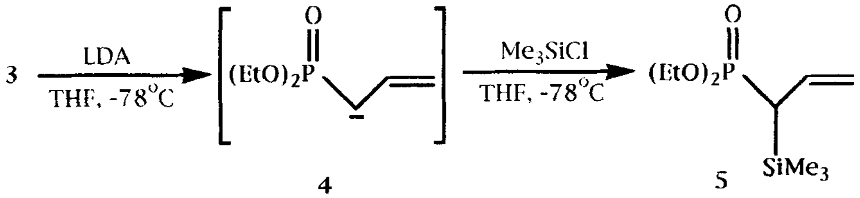
The interaction of 2-propene-1-ol (**1**) with diethylchlorophosphite in the presence of triethylamine led to formation of the allyldiethylphosphite **2**. The heating at reflux of a solution of **2** in dry xylene yielded with 65% the expected diethyl 2-propenylphosphonate **3** by [2,3]-simatropic rearrangement as shown in Scheme 1. The resulting product **3** was isolated by vacuum distillation and identified by ^1H, ^{31}P NMR, IR and mass spectra. In the ^1H NMR spectra, the signals for $H_2C{=}CH$ and CH_2 protons appear at δ 5.2-6.0 ppm as multiplet and δ 2.63 ppm as two doublets, characteristic of allylic derivatives. [4] Furthermore, the triplet and multiplet for the ethoxy group on the phosphorus were also observed. The IR spectra of **3** exhibit characteristic absorption bands for the phosphoryl group, double bond and =CH and P-O-C moieties. The data from mass spectra and the elemental analysis confirm the structure of the obtained compound.

The reaction of phosphoryl-stabilized carbanion **4** of the diethyl 2-propenylphosphonate **3**, generated *in situ* by treatment with lithium diisopropylamide (LDA), gave with trimethylchlorosilane the corresponding 1-(trimethylsilyl)-2-propenylphosphonate (**5**) with 47% yield, according to Scheme 2:

The product **5** was isolated by preparative TLC on silica gel using chloroform:ethylacetate (1:1) as an eluent. The structure of compound **5** was



Scheme 1



Scheme 2

established by ${}^1H$, ${}^{31}P$ NMR, IR and mass spectra as well as elemental analysis.

The isomerization of esters of allylphosphonic acid, promoted by base (sodium ethoxide) to esters of substituted vinylphosphonic acid has been reported. [7] The abstraction of the allylic proton in dialkyl allylphosphonate yields a secondary carbanion, which is mesomeric with a primary, and thus a more stable [5] anion. It is very likely that the primary carbanion is the major or sole contributor to the structure of the mesomeric ion, which on protonation thus yields the product derived from the most stable anion. Both anions are approximately of the same energy and protonation thus yields a mixture of the two expected products. [5] A preference for the allylic species is probably due to the electronegativity of the phosphoryl group, which stabilizes the carbanion nearest to it. [4] This is the reason for formation of α-adducts **5** as kinetic product [8, 9] in our case, probably *via* the carbanion **4** as an intermediate of the reaction.

Thus, the above results show that the diethyl 2-propenylphosphonate is a versatile reagent for the synthesis of functionalized unsaturated compounds, which could be useful as potential synthetic precursors to different monomers for polymers with valuable properties, for example incombustibility.

EXPERIMENTAL

Method of analysis

${}^1H$ NMR spectra were obtained on a JEOL JNM-FX-60 spectrometer for solutions in $CDCl_3$ operating at 60 MHz. ${}^{31}P$ NMR spectra were obtained on a BRUCKER WM-250 spectrometer for solutions in $CDCl_3$ operating at 161.9 MHz. Chemical shifts are in parts per million downfield from internal TMS (${}^1H$) and external 85% H_3PO_4 (${}^{31}P$). IR spectra were recorded with an IR-72 spectrophotometer. Elemental analyses were carried out by the University of Shoumen Microanalytical Service Laboratory.

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All reactions were carried out under an argon atmosphere and exclusion of moisture. The solvents were purified by standard methods. All compounds were checked for their purify on TLC plates.

Preparation of diethyl 2-propenylphosphonate (3)

To a solution of allylic alcohol (2-propene-1-ol) (**1**) (5.81 g, 100 mmol) and triethylamine (10.12 g, 100 mmol) in dry ether (50 ml) at −20°C was added dropwise with stirring a solution of diethylchlorophosphite (15.66 g, 100 mmol) in the same solvent (20 ml). The reaction mixture was stirred for 1 h at the same temperature and 1 h at room temperature. Then the precipiate of triethylamine hydrochloride was filtered off, the solvent was removed using a rotatory evaporator and the residue was dissolved in dry xylene (50 ml). Reflux of the solution for 5 h leads to diethyl 2-propenylphosphonate (**3**) by causing the [2,3]-sigmatropic rearrangement of the diethyl 2-propenylphosphite. After evaporation of the solvent, the residue was distilled *in vacuo* to give the pure product **3**, which had the following properties:

Yield: 65%; b.p. 72-73°C/1 mm Hg; $C_7H_{15}O_3P$, Calcd., %: P 17.39; Found, %: P 17.49. IR spectra (neat) cm^{-1}: 1012 (P-O-C), 1263 (P=O), 1642 (C=C), 3040 (=CH). ^1H NMR [6] δ: 1.11 (t, $^3J_{HH}$ 6.6 Hz, 6H, Me), 2.63 (dd, $^2J_{HP}$ 22.16 Hz, $^3J_{HH}$ 4.2 Hz, 2H, CH_2), 3.80-4.23 (m, 2H, MeCH_2O), 5.2-6.0 (m, H_2C=CH, 3H). ^{31}P NMR δ: 28.07. Mass spectra, m/z: 178 (M^+).

Preparation of diethyl 1-(trimethylsilyl)-2-propenylphosphonate (5)

To a solution of lithium diisopropylamide (LDA), generated *in situ* from diisopropylamide (DIA) (1.11g, 11 mmol) and n-butyl lithium (n-BuLi) (1.6 M in hexane, 6.25 ml, 10 mmol) in dry tetrahydrofurane (THF) (30 ml) at −78°C was added dropwise diethyl 2-propenylphosphonate (**3**) (1.78 g, 10 mmol). The reaction mixture was stirred at this temperature for 30 min. After the addition of a solution of trimethylchlorosilane (1.09 g, 10 mmol) in THF (20 ml) to the mixture, the reaction mixture was stirred at −78°C for 1 h and then at room temperature for 1 h. After that the mixture was quenched with 2N HCl, extracted with ether, washed with saturated NaCl, and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was chromatographed on silica gel using chloroform: ethylacetate (1:1) as an eluent to give the pure product **5**, which had the following properties:

yield: 47%; oil; R_f 0.51; $C_{10}H_{23}O_3PSi$, Calcd., %: P 12.37; Found, %: P 12.46. IR spectra (neat) cm^{-1}: 1025 (P-O-C), 1249 (P=O), 1631 (C=C), 3044 (=CH). ^1H NMR δ: 0.92 (t, $^3J_{HH}$ 6.3 Hz, 6H, Me), 2.26 (dd, $^2J_{HP}$ 20.61 Hz, $^3J_{HH}$ 3.7 Hz, 1H,

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CH), 3.75-4.29 (m, 2H, MeCH_2O), 5.3-6.3 (m, H_2C=CH, 3H). ^{31}P NMR δ: 32.75. Mass spectra, m/z: 250 (M^+).

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