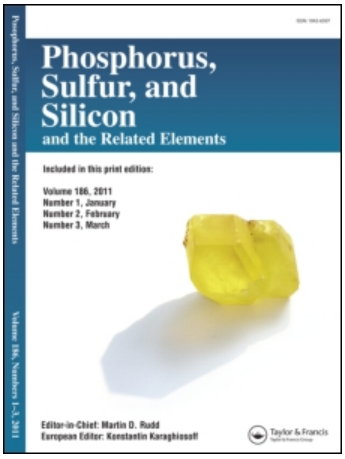

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ONE-POT SYNTHESIS OF 2-OXO-3-ALKENEPHOSPHONIC ACIDS

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Treatment of the 2-chloro-1,3-alkadienylphosphonic dichlorides **1** or acids **2** with water at reflux leads to the formation of 2-oxo-3-alkenephosphonic acids *via* the corresponding phosphorylated 1,3-alkadien-2-ols.

Keywords: 2-chloro-1,3-alkadienylphosphonic dichlorides; 2-chloro-1,3-alkadienylphosphonic acids; 2-oxo-3-alkenephosphonic acids

INTRODUCTION

Convenient methods for the preparation of phosphorylated 1,3-alkadienes were elaborated in the past twenty years,[1] thus making them available for systematic studies of their reactivity. Previously was shown that the interaction of the phosphorylated 1,3-alkadienes with electrophilic reagents[2] proceeds with cyclization of the 1,3-dienylphosphonic system with formation of heterocyclic compounds. On the other hand, we have recently reported the synthesis of the 2-chloro-1,3-alkadienylphosphonic acids by hydrolyses of 2-chloro-1,3-alkadienylphosphonic dichlorides.[3] In connection with our continuing interest in the synthetic application of the 2-chloro-1,3-alkadienylphosphonates, we have now developed an one-pot synthesis of 2-oxo-3-alkenephosphonic acids.

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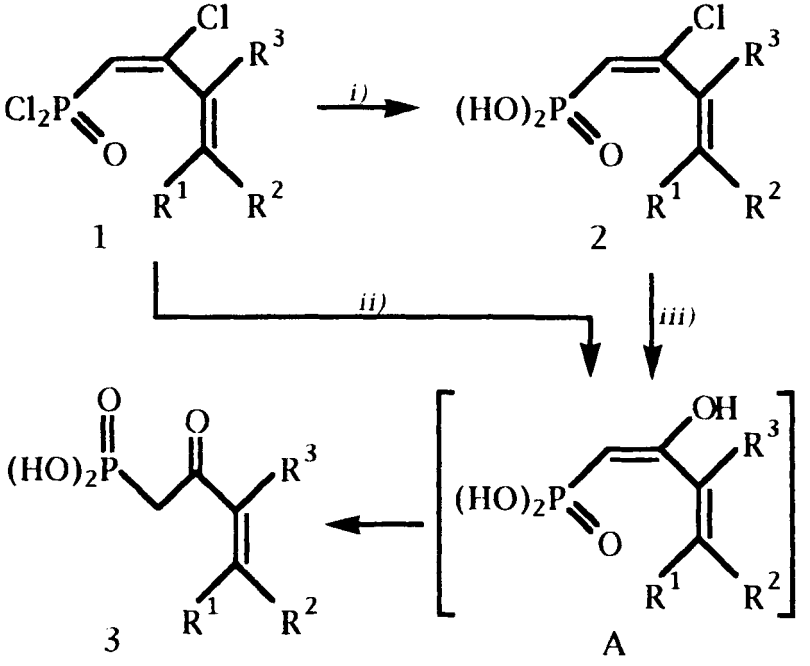
RESULTS AND DISCUSSION

We established that treatment of 2-chloro-1,3-alkadienylphosphonic dichlorides **1** with water at reflux for 2 h leads to the formation of the 2-oxo-3-alkenephosphonic acids **3** with good yield (58–62%) according to the Scheme:



1 - 3	R^1	R^2	R^3
a	H	Me	Et
b	Me	Me	Me
c	Me	Me	Pr^i

Reagents and Conditions: *i)* H_2O, acetone, reflux, 3h;[3]
ii) H_2O, reflux, 2h;
iii) H_2O, dil.HCl, reflux, 3h.

SCHEME

In a similar way, reflux of 2-chloro-1,3-alkadienylphosphonic acids **2** and water in the presence of a catalytic amount of diluted hydrochloric acid gives the same 2-oxo-3-alkenephosphonic acids **3** with better yields (65–68%)(see the **Scheme**).

The resulting products **3** were isolated by washing with hexane and water as yellow crystals and identified by ^{1}H, ^{3}C and ^{31}P NMR, IR and mass spectra as well as elemental analysis. Thus, the signal for protons of CH_2-P(δ 3.04–3.14 ppm) appears as a doublet with coupling with phosphorus ($^{2}J_{HP}$18.41–20.11 Hz) in the ^{1}NMR spectra of **3,** which is in good agreement with the literature data reported for similar compouns.[4] The 3-ethyl-2-oxo-3-pentenephosphonic acid **3a** is formed as a mixture of *(Z)*- and *(E)*-isomers, the ratio of which [*(Z)* : *(E)* = 3: 1] is determined by comparison of the intensity of the signals for the =CH proton in the ^{1}H NMR spectra. The ^{13}C NMR spectra of **3** show peaks at low field for the sp^2carbon atoms of the double bond [δ 129.01–131.33 ppm (C-4), 142.87–144.43 ppm, $^{3}J_{CP}$ 4.02–4.43 Hz (C-3)] and the carbonyl group (202.59–204.28 ppm, $^{2}J_{CP}$ 6.89–7.04 Hz) and at high field for the sp^3carbon atoms of CH_2 moiety (48.07–45.67 ppm, $^{1}J_{CP}$126.77–128.02 Hz) and the alkyl groups. The chemical shift of ^{31}P as determined with respect to 85% H_3PO_4 appears at higher field (δ14.66–16.84 ppm) than the starting material.[1a] The IR spectra of **3** exhibit characteristic absorption bands for the phosphoryl group, double bond and carbonyl group. The data from the mass spectra and the elemental analysis confirm the structure of the obtained compounds.

The simplest – although by no means unique – mechanistic rationale for the **Scheme** would appear to be *in situ* formation of the phosphorylated 1,3-alkadiene-2-ols **A** in a substitution reaction of the chlorine atom in position 2 of the 2-chloro-1,3 -alkadienylphosphonates **1** or **2** with hydroxy-group and subsequent oxo-enolic tautomerism of **A** to the 2-oxo-3-alkenephosphonic acids **3.**

The reaction reported here represents an easy approach to the phosphorylated α,β-unsaturated ketones and shows the wide applicability of the 2-chloro-1,3-alkadienylphosphonates as useful synthones in organic synthesis. Further work is in progress to examine and extend the synthetic potential of this reaction.

EXPERIMENTAL

Method of analysis

NMR spectra were obtained on a BRUCKER WM-250 spectrometer for solutions (in $CDCl_3$: d_6-DMSO = 5 : 1) operating at 250.1 (^1H), 100.6 (^{13}C) and 161.9 MH_z (^{31}P). Chemical shifts are in parts per million downfield from internal TMS (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Mass spectra were taken with a JEOL DX-300 spectrometer. IR spectra were recorded (in nujol) with an IR-72 spectrophotometer (Carl Zeiss, Jena).

Elemental analyses were carried out by the University of Shoumen Microanalytical Service Laboratory. The melting points were measured in open capillary tubes and are uncorrected.

Starting materials

2-Chloro-1,3-alkadienylphosphonic dichlorides (**1**) were synthesized by chlorination reaction of the corresponding allenylphosphonic dichlorides according to the literature.[1] 2-Chloro-1,3-alkadienylphosphonic acids (**2**) were prepared according to the established procedure.[3]

Synthesis of 2-oxo-3-alkenephosphonic acids (3)

Method a. From 2-chloro-1,3-alkadienylphosphonic dichlorides 1. General procedure

A mixture of the 2-chloro-1,3-alkadienylphosphonic dichloride **1** (5 mmol) and 5 ml distilled water was refluxed for 2h. After cooling of the solution, the product was crystallized. The pure samples were obtained by washing with hexane and water and drying in a vacuum desiccator. Yield: 58–62%.

Method b. From 2-chloro-1,3-alkadienylphosphonic acids 2. General procedure

A mixture of the 2-chloro-1,3-alkadienylphosphonic acid **2** (5 mmol), 5 ml distilled water and 1 ml diluted HCl was refluxed for 3h. After cooling of

the solution, the product was crystallized. The pure samples were obtained by washing with hexane and water and drying. Yield: 65–68%.

The products **3** had the following properties:

3-Ethyl-2-oxo-3-pentenephosphonic acid (**3a**): Yield: 58 % *(method a),* 65 % *(method b),* m.p. 109–10 °C, $C_7H_{13}O_4P$, Calcd., %: P 16.12; Found, %: P 16.21. IR spectra, cm^{-1}: 1266 (P=O), 1597 (C=C), 1687 (C=O). ^1H NMR spectra, δ: *(Z)-isomer*: 1.12 (t, 3H, $^3J_{HH}$ 8.1 Hz, $CH_2\underline{Me}$), 1.77 (dd, 3H, $^3J_{HH}$ 7.0 Hz, $^5J_{HH}$ 1.5 Hz, =CH$\underline{Me}$), 2.14–2.39 (m, 2H, $\underline{CH_2}Me$), 3.14 (d, $^2J_{HP}$ 20.11 Hz, 2H, CH_2), 6.28 (q, 1H, $^3J_{HH}$7.0 Hz, =$\underline{CH}$Me), 10.21 (s, 2HO). *(F)-isomer:* 1.06 (t, 3H, $^3J_{HH}$ 8.1 Hz, $CH_2\underline{Me}$), 1.72 (d, 3H, $^3J_{HH}$ 6.8 Hz, =CH$\underline{Me}$, 2.11–2.34 (m, 2H, $\underline{CH_2}Me$), 3.14 (d, $^2J_{HP}$20.11 Hz, 2H, CH_2), 6.36 (q, 1H, $^3J_{HH}$6.8 Hz, =C$\underline{H}$Me), 10.21 (s, 2HO). The ratio of the isomers was: *(Z)* : *(E)* = 3 : 1. ^{31}P NMR spectra, δ: 14.66. MS, m/z: 192 (M^+).

3,4-Dimethyl-2-oxo-3-pentenephosphonic acid (**3b**): Yield: 62 % *(method a),* 67 % (method b), m.p. 121–2 °C, $C_7H_{13}O_4P$, Calcd., %: P 16.12; Found, %: P 16.33. IR spectra, cm^{-1}: 1263 (P=O), 1600 (C=C), 1685 (C=O). ^1H NMR spectra, δ: 0.93 (s, 6H, $=CMe_2$), 1.21 (s, 3H, =C$\underline{Me}$), 3.11 (d, $^2J_{HP}$ 19.04 Hz, 2H, CH_2), 10.32 (s, 2H, 2HO). ^{13}C NMR spectra, δ: 22.42 (C-6), 24.56 (C-5), 30.57 (C-7), 48.07 (C-1, $^1J_{CP}$ 128.02 Hz), 131.33 (C-4), 144.43 (C-3, $^3J_{CP}$ 4.43 Hz), 204.28 (C-2, $^2J_{CP}$ 6.89 Hz). ^{31}P NMR spectra, δ: 16.84. MS, m/z: 192 (M^+).

3-Isopropyl-4-methyl-2-oxo-3-pentenephosphonic acid (**3c**): Yield: 62 % *(method a),* 68 % *(method b),* m.p. 135–6 °C; $C_9H_{17}O_4P$, Calcd., %: P 14.07; Found, %: P 14.23. IR spectra, cm^{-1}: 1268 (P=O), 1602 (C=C), 1683 (C=O). ^1H NMR spectra, δ: 1.02 (s, 6H, $=C\underline{Me_2}$), 1.64 (d, $^3J_{HH}$16.0 Hz, 6H, $CH\underline{Me_2}$), 2.72 (m, 1H,$C\underline{H}Me_2$), 3.04 (d, $^2J_{HP}$ 18.41 Hz, 2H, CH_2), 9.98 (s, 2H, 2HO). ^{13}C NMR spectra, δ: 19.47 (C-9), 21.23 (C-6), 21.97 (C-8), 22.06 (C-5), 28.40 (C-7), 45.67 (C-1, $^1J_{CP}$ 126.77 Hz), 129.01 (C-4), 142.87 (C-3, $^3J_{CP}$ 4.02 Hz), 202.59 (C-2, $^2J_{CP}$ 7.04 Hz). ^{31}P NMR spectra, δ:15.25. MS, m/z: 220 (M^+).

Acknowledgements

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