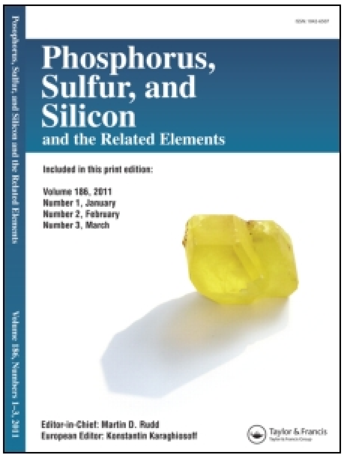

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HYDRATION REACTIONS OF PHOSPHORYLATED 1,3-ENYNES

Valerij Ch. Christov[a]; Veneta M. Aladinova[b]; Boris Prodanov[a]
[a] Department of Chemistry, University of Shoumen, Shoumen, Bulgaria [b] Department of Biology & Chemistry, Pedagogical Institute, Silistra, Bulgaria

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HYDRATION REACTIONS OF PHOSPHORYLATED 1,3-ENYNES[1]

VALERIJ CH. CHRISTOV[a*], VENETA M. ALADINOVA[b] and
BORIS PRODANOV[a]

[a]Department of Chemistry, University of Shoumen, BG-9700 Shoumen, Bulgaria and [b]Department of Biology & Chemistry, Pedagogical Institute, BG-7500 Silistra, Bulgaria

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Hydration of the 3-alkene-1-ynephosphonic dimethyl esters **3** in the presence of a mixture of mercuric sulfate and sulfuric acid as a catalyst takes place with addition of water to the triple bond and hydrolysis of the phosphonate group with formation of the 2-oxo-3-alkenephosphonic acids **4**. Ketalation of the 3-alkene-1-ynephosphonic dimethyl esters **3** with methanol using as a catalyst a mixture of yellow mercuric oxide, trichloroacetic acid and boron trifluoride etherate and subsequent hydrolysis of the prepared phosphorylated ketals **B** leads to the 2-oxo-3-alkenephosphonic dimethyl esters **5**. Treatment of **3** with water in the presence of concentrated hydrochloric acid yields the 3-alkene-1-ynephosphonic acids **6**.

Keywords: 3-alkene-1-ynephosphonic dimethyl esters; mercuric catalysts; hydration; hydrolysis; 2-oxo-3-alkenephosphonic acids; ketalation; 2-oxo-3-alkenephosphonic dimethyl esters; 3-alkene-1-ynephosphonic acids

INTRODUCTION

It was shown the wide applicability of the 2-chloro-1,3-alkadienylphosphonates for the synthesis of five- or six-membered heterocyclic compounds,[2a] or mixtures of them,[2b]3-alkene-1-ynephosphonic dichlorides and difluorides,[2c, 2d] 1,2,2,3-tetrahalogeno-alkanephosphonic acids,[2e] alkenephosphonic esters,[2b, 2f] 2-oxo-3 -alkenephosphonic acids[12] etc.

On the other hand, the hydration of triple bonds is generally carried out with mercuric ion salts (often the sulfate or acetate) as catalysts.[3] Mercuric oxide in the presence of acid is also a common reagent.[4] Since the

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* Corresponding author. E-Mail: vchristo@main.uni-shoumen.acad.bg

addition follows Markovnikov's rule, only acetylene gives an aldehyde. All other triple-bond compounds give ketones. The reaction can be conveniently carried out with a catalyst prepared by impregnating mercuric oxide onto Naflon-H (a superacidic perfluorinated resinsulfonic acid).[5] The first step of the mechanism is formation of a complex between the triple bond and Hg^{2+}. Water then attacks in a S_N2-type process to give a mercury-containing intermediate. Its hydrolysis gives an enol, which tautomerizes to the ketone.[4] Moreover, certain alkynes have also been hydrated to ketones with acid in the absence of mercuric catalyst.[6] This is ordinary electrophilic addition, with rate-determining protonation as the first step.[7]

The addition of alcohols and phenols to double and triple bonds is catalyzed by acids or bases. When the reactions are acid-catalyzed, the mechanism is electrophilic with H^+ as the attacking species. The addition follows Markovnikov's rule.[4] For those substrates more susceptible to nucleophilic attack, it is better to carry out the reaction in basic solution, where the attacking species is RO^-.[8] Since triple bonds are more susceptible to nucleophilic attack than double bonds, it might be expected that bases would catalyze addition of alcohols to triple bonds particularly well. This is the case, and enol ethers and acetals (ketals) can be produced by this reaction.[9] Because enol ethers are more susceptible than triple bonds to electrophilic attack, the addition of alcohols to enol ethers can also be catalyzed by acids.[10] Other catalysts, namely, boron trifluoride and mercuric oxide, have also been used in the addition of alcohols to triple bonds.[4] The 1,3-enynes have been studied much less but behave similarly – the reagent attacks the triple bond with formation of α,β-unsaturated ketones.[11] Hydration and addition reaction of alcohols to phosphorylated 1,3-enynes have not been investigated to date.

We have previously reported[12] a convenient one-pot synthesis of 2-oxo-3-alkenephosphonic acids by the treatment of 2-chloro-1,3-alkadienylphosphonates with water at reflux.

As a part of our continuing study on the chemistry of the phosphorylated 1,3-alkadienes, we report[13] here the results on the synthetic application of these compounds for preparation of phosphorylated 1,3-enynes and investigation of their hydration reactions. Preparative procedures including full characterization of the prepared 2-oxo-3-alkenephosphonic acids and dimethyl esters as well as the 3-alkene-1-ynephosphonic acids are presented here.

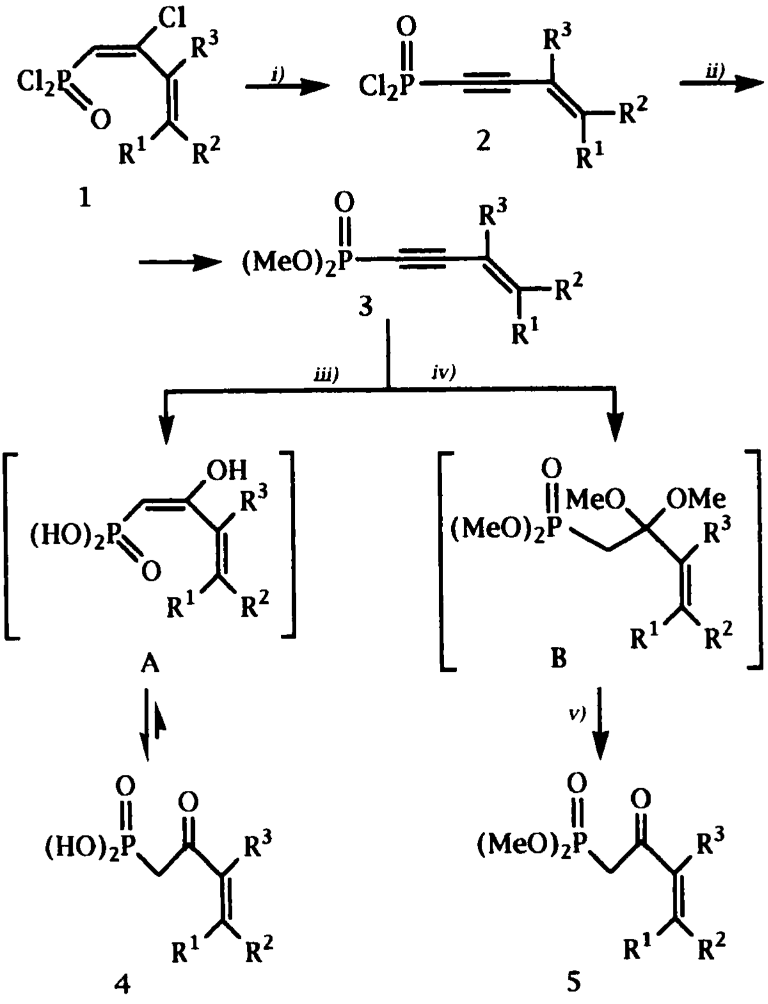
RESULTS AND DISCUSSION

Using the 2-chloro-1,3-alkadienylphosphonic dichlorides **1** as starting materials, the 3-alkene-1-ynephosphonic dimethyl esters **3** were prepared by elimination reaction[2c, 2d] of hydrogen chloride in benzene at reflux with formation of the corresponding dichlorides **2** (76–82 % yield) and subsequent substitution reaction of the two chlorine atoms with methanol in the presence of pyridine (66–76 % yield) as shown in the **Scheme 1**.

The phosphorylated 1,3-enynes **3** obtained in preparative amounts allowed us to study their hydration reactions. If we used the above mentioned mercuric catalysts containing water in strong acidic conditions, together with hydration of the triple bond of the 3-alkene-1-ynephosphonic dimethyl esters **3**, a hydrolysis of the phosphonate group would occur with formation of the corresponding phosphonic acids. Really, the treatment of the 3-alkene-1-ynephosphonic dimethyl esters **3** with water in the presence of a mixture of mercuric sulfate and sulfuric acid as a catalyst at 80–90 °C led to the phosphorylated 1,3-alkadiene-2-ols **A**, which tautomerized into the 2-oxo-3-alkenephosphonic acids **4** with good yields (57–63%) **(Scheme 1)**. The reaction is highly regioselective to give a single product in each of the cases that we have studied. The acids **4** were isolated by crystalization as white crystals and their structure was assigned on the basis of their ^{1}H, ^{13}C NMR and IR spectra as well as elemental analysis in accordance with a literature report.[12]

Thus, our first problem was to find suitable conditions for hydration of the phosphorylated 1,3-enynes without hydrolysis of phosphonate group using a mercuric catalyst in strong acidic but non-aqueous conditions in order to obtain only hydration products. This problem was solved by using a mixture of yellow mercuric oxide, trichloroacetic acid and boron trifluoride etherate as a catalyst in the ketalation reaction of the phosphorylated 1,3-enynes. We established that the ketalation reaction of the 3-alkene-1-ynephosphonic dimethyl esters **3** with methanol at reflux using as a catalyst a pre-heated (to 60 °C) mixture of yellow mercuric oxide, trichloroacetic acid and boron trifluoride etherate yielded the phosphorylated ketals **B (Scheme 1).**

The second problem was to find suitable conditions for transformation of the phosphorylated ketals **B** to the corresponding hydration products. It is known that the acetals and ketals are easily cleaved by dilute acids.[17] It has been shown that at least three mechanisms can take place with those



1-5	R^1	R^2	R^3
a	H	Me	Et
b	H	$-(CH_2)_4-$	
c	Me	Me	Me
d	Me	Me	Pr^i

Reagents and Conditions:

i) Et_3N, benzene, reflux, 2h;
ii) MeOH, pyridine, ether, 0-10 °C, 1h;
iii) $HgSO_4$, H_2SO_4, H_2O, 80-90 °C, 5h;
iv) HgO, CCl_3COOH, $BF_3.Et_2O$, MeOH, reflux, 6h;
v) H_2O, 2N HCl, rt.

SCHEME 1

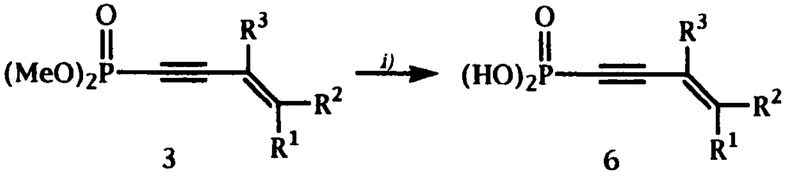
substrates in the hydrolysis reaction[18] – for example: S_N1cA,[19a] S_N2cA,[19b] or A-S_E2.[19c] The problem was solved by hydrolysis of the ketals **B** in the presence of dilute hydrochloric acid[20] at room temperature which gave the 2-oxo-3-alkenephosphonic dimethyl esters 5 with good yields (63–69%). The reaction is highly regioselective to give a single product in each of the cases that we have studied. The resulting products **5** were isolated by preparative TLC as light yellow oils and identified by ^1H, ^{13}C NMR and IR spectra as well as elemental analysis. Thus, in the ^1H NMR spectra of **5**, the signal for protons of the CH_2-P moiety (δ 3.11–3.25 ppm) appears as a doublet with coupling with phosphorus ($^2J_{HP}$ 19.80–22.10 Hz), which is in good agreement with the literature data for similar compounds.[12, 16] The 3-ethyl-2-oxo-3-pentenephosphonic dimethyl esters **5a** is formed as a mixture of *(Z)*-and *(E)*-isomers, the ratio of which [*(Z)*: *(E)* = 2.7: 1] is determined by comparison of the intensity of the signals for the =<u>CH</u>Me proton [δ 6.24 ppm for *(Z)*- and 6.30 ppm for *(E)*-isomer] in the ^1H NMR spectra. In the ^{13}C NMR spectra of **5**, the C-1 carbon atom is a doublet signal in high field (δ 47.18–49.11 ppm) whose coupling constant between carbon and phosphorus ($^1J_{CP}$ 129.88–130.15 Hz) is fully in accord with that reported for the corresponding acids.[12] Moreover, the ^{13}C NMR spectra of **5** show peaks at low field for the sp^2 carbon atoms of the double bond [δ 139.94–143.7 ppm, $^3J_{CP}$ 4.75–4.86 Hz (C-3) and 131.45–134.66 ppm (C-4)] and the carbonyl group (δ 206.87–207.64 ppm, $^2J_{CP}$7.24–7.82 Hz) and at high field for the sp^3 carbon atoms of the methoxy and alkyl groups. The IR spectra of **5** exibit characteristic absorption bands for the phosphoryl group, double bond and carbonyl group. The data from the elemental analysis confirm the structure of the compounds prepared.

The reaction of the 3-alkene-1-ynephosphonic dimethyl esters **3** with water in the presence of hydrochloric acid finished hydrolysis with formation of the corresponding 1,3-enynephosphonic acids **6 (Scheme 2),** but no hydration, i. e. the hydration reaction of the 3-alkene-1-ynephosphonic dimethyl esters **3** without mercuric catalyst did not occur (**Scheme 2**).

In conclusion, we note the following points from this investigation:

i. the hydration reactions of the 3-alkene-1-ynephosphonates catalyzed by mercuric compounds represent an easy approach to the phosphorylated 3-alkene-2-ones;

ii. the hydration reactions of the phosphorylated 1,3-enynes in the absence of mercuric catalyst do not occur;



3, 6	R^1	R^2	R^3
b	H	-(CH$_2$)$_4$-	
c	Me	Me	Me
d	Me	Me	Pr^i

Reagents and Conditions:
i) H_2O, conc.HCl, 60-70°C, 5h;

SCHEME 2

iii. an interesting synthetic transition between phosphorylated compounds is realized: from 1,3-alkadienes through 1,3-alkenynes to 3-alkene-2-ones; and

iv. the 2-chloro-1,3-alkadienylphosphonates are versatile synthones in organic synthesis.

EXPERIMENTAL

Method of analysis

NMR spectra were obtained on a BRUCKER WM-250 spectrometer for solutions in $CDCl_3$ or ($CDCl_3$: d_6-DMSO = 5:1) operating at 250.1 (^1H), 100.6 (^{13}C) and 161.9 MHz (^{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).

IR spectra were recorded with an IR-72 spectrophotometer (Carl Zeiss, Jena). Elemental analyses were carried out by the University of Shoumen Microanalytical Service Laboratory.

The boiling points are uncorrected. The melting points were measured in open capillary tubes and are uncorrected. The solvents were purified by standard methods. Ketalation reactions were carried out in oven-dried glassware under an argon atmosphere and exclusion of moisture. All compounds were checked for their purify on TLC plates.

Starting materials

2-Chloro-1,3-alkadienylphosphonic dichlorides (**1**) were synthesized by chlorination reaction of allenylphosphonic dichlorides according to the literature.[15]

3-Alkene-1-ynephosphonic dichlorides (2)

were prepared from the 2-chloro-1,3-alkadienylphosphonic dichlorides **1** by a procedure described earlier.[2c, 15b]

3-Ethyl-3-pentene-1-ynephosphonic dichloride (2a)

Yield: 77 %; b.p. 121–3 °C/0.5 mm Hg; $C_7H_9OPCl_2$, Calcd., %: P 14.68, Cl 33.60; Found, %: P 14.54, Cl 33.76 IR spectra (neat), cm^{-1}: 1286 (P=O), 1621 (C=C), 2152 (C≡C). ^1H NMR spectra ($CDCl_3$), δ: *(Z)-isomer:* 1.09 (t, 3H, $^3J_{HH}$ 8.7 Hz, $CH_2\underline{Me}$), 1.87 (dd, 3H, $^3J_{HH}$ 7.6 Hz, $^5J_{HH}$ 1.6 Hz, $=CH\underline{Me}$), 2.11–2.42 (m, 2H, $\underline{CH_2}Me$), 3.24 (d, $^2J_{HP}$ 21.8 Hz, 2H, CH_2), 6.29 (q, 1H, $^3J_{HH}$ 6.6 Hz, $=C\underline{H}Me$). *(E)-isomer:* 0.98 (t, 3H, $^3J_{HH}$ 8.5 Hz, $CH_2\underline{Me}$), 1.74 (d, 3H, $^3J_{HH}$ 6.8 Hz, $=CH\underline{Me}$), 2.14–2.47 (m, 2H, $\underline{CH_2}Me$), 3.30 (d, $^2J_{HP}$ 21.2 Hz, 2H, CH_2), 6.47 (q, 1H, $^3J_{HH}$ 5.8 Hz, $=C\underline{H}Me$). The ratio of the isomers was: *(Z)*: *(E)* = 2.8: 1.

3-Isopropyl-4-methyl-3-pentene-1-ynephosphonic dichloride (2d)

Yield: 82 %; b.p. 141–2 °C/0.5 mm Hg; $C_9H_{13}OPCl_2$, Calcd., %: P 12.96, Cl 29.66; Found, %: P 13.17, Cl 29.81. IR spectra (neat), cm^{-1}: 1284 (P=O), 1623 (C=C), 2154 (C≡C). ^1H NMR spectra ($CDCl_3$), δ: 1.84, 2.02 (s, s, 6H, $=C\underline{Me_2}$), 1.73 (d, $^3J_{HH}$ 14.4 Hz, 6H, $CH\underline{Me_2}$), 2.87 (m, 1H, $C\underline{H}Me_2$).

The products **2b-c** are known compounds whose spectroscopic properties were fully in accord with those reported.[2c, 15b]

Synthesis of 3-alkene-1-ynephosphonic dimethyl esters (3). General procedure

To a solution of the 3-alkene-1-ynephosphonic dichloride **2** (10 mmol) in dry diethyl ether (30 ml) at 0–5 °C was added dropwise with stirring a solution of the mixture of methanol (20 mmol) and pyridine (20 mmol) in the same solvent (10 ml). The stirring was continued for 1h at the same temperature. Then the precipitate of pyridine hydrochloride was filtered off, the solvent was removed using a rotatory evaporator and the residue was distilled under vacuum to give the pure products as a light yellow liquid. Yield: 66–76 %. The products **3** had the following properties:

3-Ethyl-3-pentene-1-ynephosphonic dimethyl ester (3a)

Yield: 68 %; b.p. 133–4 °C/0.5 mm Hg; $C_9H_{15}O_3P$, Calcd., %: P 15.32; Found, %: P 15.47. IR spectra (neat), cm^{-1}: 1246 (P=O), 1609 (C=C), 2142 (C≡C). ^1H NMR spectra ($CDCl_3$), δ: *(Z)-isomer:* 1.07 (t, 3H, $^3J_{HH}$ 8.7 Hz, $CH_2\underline{Me}$), 1.84 (dd, 3H, $^3J_{HH}$ 7.4 Hz, $^5J_{HH}$ 1.3 Hz, $=CH\underline{Me}$), 2.09–2.45 (m, 2H, $\underline{CH_2}Me$), 3.27 (d, $^2J_{HP}$ 21.2 Hz, 2H, CH_2), 3.68 (d, $^3J_{HP}$ 10.4 Hz, 6H, 2MeO), 6.32 (q, 1H, $^3J_{HH}$ 6.6 Hz, $=C\underline{H}Me$). *(E)-isomer:* 0.96 (t, 3H, $^3J_{HH}$ 8.3 Hz, $CH_2\underline{Me}$), 1.72 (d, 3H, $^3J_{HH}$ 6.8 Hz, $=CH\underline{Me}$), 2.11–2.53 (m, 2H, $\underline{CH_2}Me$), 3.27 (d, $^2J_{HP}$ 21.2 Hz, 2H, CH_2), 3.68 (d, $^3J_{HP}$ 10.4 Hz, 6H, 2MeO), 6.44 (q, 1H, $^3J_{HH}$ 6.0 Hz, $=C\underline{H}Me$). The ratio of the isomers was: *(Z)*:*(E)* = 2.8:1.

2(1-Cylcohexenyl) ethynephosphonic dimethyl ester (3b)

Yield: 66 %; b.p. 154–5 °C/1.0 mm Hg; $C_{10}H_{15}O_3P$, Calcd., %: P 14.46; Found, %: P 14.61. IR spectra (neat), cm^{-1}: 1254 (P=O), 1612 (C=C), 2150 (C≡C), ^1H NMR spectra ($CDCl_3$), δ: 1.54, 2.05, 6.43 (s, s, m, 9H, cyclohexenyl), 3.65 (d, $^3J_{HP}$ 10.3 Hz, 6H, 2MeO).

3,4-Dimethyl-3-pentene-1-ynephosphonic dimethyl ester (3c)

Yield: 76 %; b.p. 137–8 °C/1.0 mm Hg; $C_9H_{15}O_3P$, Calcd., %: P 15.32; Found, %: P 15.43. IR spectra (neat), cm^{-1}: 1244 (P=O), 1610 (C=C), 2146 (C≡C). ^1H NMR spectra ($CDCl_3$), δ: 1.84, 2.02 (s, s, 9H, $\underline{Me}C=C\underline{Me_2}$), 3.62 (d, $^3J_{HP}$ 10.8 Hz, 6H, 2MeO).

3-Isopropyl-4-methyl-3-pentene-1-ynephosphonic dimethyl ester (3d)

Yield: 74 %; b.p. 136–7 °C/0.3 mm Hg; $C_{11}H_{19}O_3P$, Calcd., %: P 13.45; Found, %: P 13.51. IR spectra (neat), cm^{-1}: 1246 (P=O), 1613 (C=C), 2146 (C≡C). ^1H NMR spectra ($CDCl_3$), δ: 1.76, (s, 6H, $=C\underline{Me_2}$), 1.89 (d, $^3J_{HH}$ 13.7 Hz, 6H, $CH\underline{Me_2}$), 2.74–2.90 (m, 1H,$C\underline{H}Me_2$), 3.58 (d, $^3J_{HP}$ 9.87 Hz, 6H, 2MeO).

Hydration and hydrolysis of 3-alkene-1-ynephosphonic dimethyl esters (3). General procedure

A mixture of mercuric sulfate (0.08 g), concentrated sulfuric acid (0.08 ml) and distilled water (2 ml) was heated at 80 °C for 5 min. To the prepared catalyst was added dropwise with stirring the 3-alkene-1-ynephosphonic dimethyl esters (**3**) (5 mmol). The reaction mixture was heated at 80–90 °C for 5 h and then at room temperature for 1 h. Then the reaction mixture was washed with water and extracted with dichloromethane. The water layer was washed with brine and extracted with dichloromethane. The united organic layers were dried over anhydrous sodium sulfate. Then the solvent was removed using a rotatory evaporator. After cooling, the product was crystallized. The pure samples were obtained by washing with hexane and drying. Yield: 57–63 %.

The physical and IR and NMR spectral data of the *3-ethyl-2-oxo-3-pentene-phosphonic acid* **4a** [yield: 60 %, the ratio of the isomers: *(Z)*: *(E)*= 2.5: 1)], the *3,4-dimethyl-2-oxo-3-pentenephosphonic acid* **4c** (yield: 63 %) and the *3-isopropyl-4-methyl-2-oxo-3-pentenephosphonic acid* **4d** (yield: 58 %) were in good agreement with the literature data for those compounds.[12]

2-Oxo-2(1-cyclohexenyl) ethanephosphonic acid (4b)

Yield: 57 %; m.p. 141–2 °C; $C_8H_{13}O_4P$, Calcd., %: P 15.17; Found, %: P 15.26. IR spectra (nujol), cm^{-1}: 1264 (P=O), 1601 (C=C), 1680 (C=O), ^1H NMR spectra ($CDCl_3$: d_6-DMSO = 5: 1), δ: 1.69, 2.14, 5.98–6.16 (s, s, m, 9H, cyclohexenyl), 3.18 (d, $^2J_{HP}$ 21.11 Hz, 2H, CH_2), 11.04 (s, 2H, 2HO).

Ketalation and subsequent hydrolysis of 3-alkene-1-ynephosphonic dimethyl esters(3). General procedure

A mixture[14] of yellow mercuric oxide (100 mg), trichloroacetic acid (25 mg), boron trifluoride etherate (0.15 mg) and dry methanol (0.25 ml) was heated at 60 °C for 3 min. To the prepared catalyst was added dropwise with stirring the 3-alkene-1-ynephosphonic dimethyl esters (**3**) (5 mmol). The reaction mixture was heated at 60–70 °C for 6 h and then at room temperature for 1 h. After the reaction mixture was washed with water and 2N hydrochloric acid and extracted with diethyl ether. The water layer was washed with brine and extracted with ether. The united organic layers were dried over anhydrous sodium sulfate. Then the solvent was removed using a rotatory evaporator. The residue was chromatographed on preparative TLC with hexane and ethyl acetate as a eluent to give the 2-oxo-3-alkenephosphonic dimethyl esters **5**. Yield: 63–69 %. The products **5** had the following properties:

3-Ethyl-2-oxo-3-pentenephosphonic dimethyl esters (5a)

Yield: 67 %, oil, $C_9H_{17}O_4P$, Calcd., %: P 14.07; Found, %: P 14.20. IR spectra, cm^{-1}: 1273 (P=O), 1595 (C=C), 1689 (C=O). ^1H NMR spectra ($CDCl_3$), δ: *(Z)-isomer:*1.06 t, 3H, $^3J_{HH}$ 7.7 Hz, $CH_2\underline{Me}$), 1.72 (dd, 3H, $^3J_{HH}$ 6.8 Hz, $^5J_{HH}$ 1.6 Hz, $=CH\underline{Me}$), 2.03–2.27 (m, 2H, $\underline{CH_2}Me$), 3.11 (d, $^2J_{HP}$ 19.81 Hz, 2H, CH_2), 3.52 (d, $^3J_{HP}$ 9.4 Hz, 6H, 2MeO), 6.24 (q, 1H, $^3J_{HH}$ 7.1 Hz, $=C\underline{H}Me$). *(E)-isomer:* 1.03 (t, 3H, $^3J_{HH}$ 7.7 Hz, $CH_2\underline{Me}$), 1.67 (d, 3H, $^3J_{HH}$ 6.7 Hz, $=CH\underline{Me}$), 2.00–2.25 (m, 2H, $\underline{CH_2}Me$), 3.11 (d, $^2J_{HP}$ 19.8 Hz, 2H, CH_2), 3.52 (d, $^3J_{HP}$ 9.4 Hz, 6H, 2MeO), 6.30 (q, 1H, $^3J_{HH}$ 6.8 Hz, $=C\underline{H}Me$). The ratio of the isomers was: *(Z): (E)* = 2.7: 1. ^{31}P NMR spectra, δ: 17.34.

2-Oxo-2(1-cyclohexenyl) ethanephosphonic dimethyl esters (5b)

Yield: 63 %, oil, $C_{10}H_{17}O_4P$, Calcd., %: P 13.34; Found, %: P 13.41. IR spectra, cm^{-1}: 1275 (P=O), 1592 (C=C), 1691 (C=O). ^1H NMR spectra ($CDCl_3$), δ: 1.61, 2.09, 6.04–6.31 (s, s, m, 9H, cyclohexenyl), 3.25 (d, $^2J_{HP}$ 22.1 Hz, 2H, CH_2), 3.69 (d, $^3J_{HP}$ 10.9 Hz, 6H, 2MeO).

3,4-Dimethyl-2-oxo-3-pentenephosphonic dimethyl esters (5c)

Yield: 69 %, oil, $C_9H_{17}O_4P$, Calcd., %: P 14.07; Found, %: P 14.02. IR spectra, cm^{-1}: 1269 (P=O), 1597 (C=C), 1685 (C=O).^1H NMR spectra ($CDCl_3$), δ: 0.90 (s, 6H, $=C\underline{Me_2}$), 1.23 (s, 3H, $=C\underline{Me}$), 3.24 (d, $^2J_{HP}$ 20.0 Hz, 2H, CH_2), 3.63 (d, $^3J_{HP}$ 9.6 Hz, 6H, 2MeO). ^{13}C NMR spectra, δ: 21.33 (C-6), 24.11 (C-5), 28.60 (C-7), 49.11 (C-1, $^1J_{CP}$ 130.15 Hz), 56.35 (C-8, $^2J_{CP}$ 6.78 Hz), 134.66 (C-4), 143.7 (C-3, $^3J_{CP}$ 4.75 Hz), 206.87 (C-2, $^2J_{CP}$ 7.24 Hz). ^{31}P NMR spectra, δ: 18.47.

3-Isopropyl-4-methyl-2-oxo-3-pentenephosphonic dimethyl esters (5d)

Yield: 64 %, oil, $C_{11}H_{21}O_4P$, Calcd., %: P 12.48; Found, %: P 12.53. IR spectra, cm^{-1}: 1272 (P=O), 1600 (C=C), 1686 (C=O). ^1H NMR spectra ($CDCl_3$), δ: 1.07 (s, 6H, $=C\underline{Me_2}$), 1.82 (d, $^3J_{HH}$ 16.8 Hz, 6H, $CH\underline{Me_2}$), 2.88 (m, 1H, $C\underline{H}Me_2$), 3.24 (d, $^2J_{HP}$ 19.84 Hz, 2H, CH_2), 3.68 (d, $^3J_{HP}$

9.5 Hz, 6H, 2MeO). ^{13}C NMR spectra, δ: 20.18 (C-9), 22.04 (C-6), 22.79 (C-8), 24.08 (C-5), 27.54 (C-7), 47.18 (C-1, $^{1}J_{CP}$ 129.88 Hz), 61.08 (C-10, $^{2}J_{CP}$ 7.03 Hz), 131.45 (C-4), 139.94 (C-3, $^{3}J_{CP}$ 4.86 Hz), 207.64 (C-2, $^{2}J_{CP}$ 7.82 Hz). ^{31}P NMR spectra, δ: 16.48.

Hydrolysis of 3-alkene-1-ynephosphonic dimethyl esters (3). General procedure

A mixture of the 3-alkene-1-ynephosphonic dimethyl esters (**3**) (5 mmol), water (6 mmol) and concentrated hydrochloric acid (3 ml) was heated at 60–70 °C for 5 h and then at room temperature for 1 h. After cooling, the product was crystallized. Then the residue was filtered, dried and recrystallized from heptane to give the pure products as white crystals. Yield: 53–60 %. The products **6** had the following properties:

2(1-Cylcohexenyl) ethynephosphonic acid (6b)

Yield: 53 %; m.p. 94–5 °C; $C_8H_{11}O_3P$, Calcd., %: P 16.64; Found, %: P 16.82. IR spectra (nujol), cm^{-1}: 1275 (P=O), 1623 (C=C), 2159 (C≡C). ^{1}H NMR spectra ($CDCl_3$: d_6-DMSO = 5: 1), δ: 1.49, 2.13, 6.54 (s, s, m, 9H, cyclohexenyl), 10.03 (s, 2H, 2HO).

3,4-Dimethyl-3-pentene-1-ynephosphonic acid (6c)

Yield: 60 %; m.p. 73–4 °C; $C_7H_{11}O_3P$, Calcd., %: P 17.79; Found, %: P 18.04. IR spectra (nujol), cm^{-1}: 1274 (P=O), 1620 (C=C), 2152 (C≡C). ^{1}H NMR spectra ($CDCl_3$: d_6-DMSO = 5: 1), δ: 1.78, 1.98 (s, s, 9H, $\underline{Me}C{=}C\underline{Me_2}$), 9.76 (s, 2H, 2HO).

3-Isopropyl-4-methyl-3-pentene-1-ynephosphonic acid (6d)

Yield: 57 %; m.p. 77–8 °C; $C_9H_{15}O_3P$, Calcd., %: P 15.32; Found, %: P 15.45. IR spectra (nujol), cm^{-1}: 1276 (P=O), 1619 (C=C), 2156 (C≡C). ^{1}H NMR spectra ($CDCl_3$: d_6-DMSO = 5: 1), δ: 1.88 (s, 6H, $=C\underline{Me_2}$), 1.94 (d, $^{3}J_{HH}$ 14.6 Hz, 6H, $CH\underline{Me_2}$), 2.79–2.94 (m, 1H, $C\underline{H}Me_2$), 9.34 (s, 2H, 2HO).

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References

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