Heteroatom Chemistry
Volume 6, Number 6, 1995

3-Silanyl-Propenylphosphonates: Properties and Alkylation Potential

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Received 14 February 1995; revised 5 April 1995

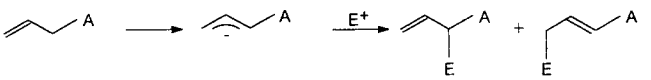
ABSTRACT

*Two 3-silanyl-propenylphosphonate esters (**1a**, **1b**) were synthesized, and their deprotonation was attempted using RONa/ROH, RLi/THF, and LDA/THF systems. In the first two cases, the nucleophilic addition was the predominant (or exclusive) reaction observed; deprotonation was achieved with LDA, as confirmed by the reaction of the lithiated species with alkylating agents and with benzaldehyde. Chemical behavior of substrates* **1** *does not parallel closely that of the parent silanyl or phosphoryl-substituted allylic systems.* © *1996 John Wiley & Sons, Inc.*

INTRODUCTION

Carbanions generated from allylphosphonates [1] or from allylsilanes [2] have been used for the preparation of dienes and polyenes via olefination reactions with electrophiles like aldehydes or ketones [3,4]. From the regioselectivity point of view, the condensation reactions occur usually exclusively at the carbon α to a heteroatom; however, in cases of bulkier electrophiles, the isomeric γ product may become favored (Scheme 1).

Allylphosphonates can be easily deprotonated with alkyllithium bases. In reactions with alkyl halides, electrophilic substitution takes place, in a kinetically controlled process, at the α position. But, in cases of Me_3SiCl as an electrophile, the γ product was exclusively obtained [5], which indicates that steric effects play an important role in the regioselectivity of the substitution reactions. The success in the preparation of dienes via the Wittig–Horner reaction with lithiated allylphosphonates as substrates depends on the relative configuration of the two chiral centers in the diastereomeric aldehyde adducts [6]. In similar reactions of silanyl-stabilized carbanions, the regioselectivity depends more on the substitution at silicon, and by changing those substituents, the α substitution can be changed into the γ substitution [7]. In this work, we report on the behavior of two silanyl-propenylphosphonates; i.e., the allylic derivatives with the diethoxyphosphonyl and the trialkylsilyl substituents located at the 1,3-position of the allylic system. After lithiation, those substrates yield an allylic carbanion stabilized by two heteroatoms, and the reactivity of such systems should be determined by the relative effects of phosphorus and silicon on the adjacent carbanionic center and on the incipient olefinic bond.



A= PO_3Et_2 or SiR_3

SCHEME 1

RESULTS AND DISCUSSION

The preparation of silanyl-propenylphosphates (**1a,b**) was based on the reported [5] reaction of lithiated allylphosphonate with Me_3SiCl at $-78°C$. ^{31}P and ^1H-NMR spectra of the crude reaction mixture showed the exclusive formation of the γ-substituted product (Scheme 2).

Both products **1** are formed exclusively as *E* ster-

Dedicated to Prof. Dr. Hans-Georg Horn on the occasion of his sixtieth birthday.

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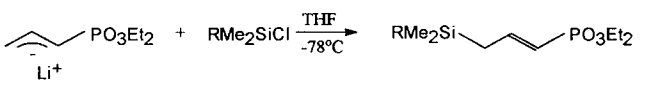
1042-7163/96/060579-06

eoisomers and can be separated from starting materials by distillation (more effective for **1b** because of the bigger difference in the respective boiling points). It was noticed, however, that in some cases, particularly when the electrophile was added to the lithiated derivative at a faster rate, or when the distillation of the product was carried out slowly, two additional products (**2a,b** or **3a,b**) could be detected by ^{31}P NMR spectroscopy. The maximum content of those side products was ca. 20% for **1a** and 13% for **1b**; the ratios **2a/2b** and **3a/3b** were usually ca. 2:1, and sometimes products **3a** and **3b** could not be detected. In order to identify products **2** and **3**, the primary products **1** were heated in sealed tubes at 120°C until at least 60% of their conversion to **2** (or **3**) was achieved (two days). No **1a** → **2a/3a** or **1b** → **2b/3b** conversion was observed upon irradiation with UV light. After separation and purification, **2** and **3** were identified as the (*E*) or (*Z*) products of the isomerization of **1** with the olefinic bond shifted to the $\alpha'\beta'$ position with respect to silicon (Scheme 3).

It is obvious that compounds **2** and **3** cannot be formed directly in the reaction of the lithiated allylphosphonate and RMe_2SiCl, but are the products of thermal isomerization of **1** (occurring partially also during the distillation or as result of a local overheating of the initial reaction mixture). The transformation of **1** → **2(3)** represents a 1,3-sigmatropic shift within an allylic system. Usually allylsilanes are regiostable and undergo a 1,3-shift at temperatures above 300°C [8]. The phosphonyl substituent at the other terminal of the system obviously lowers the activation energy of the shift; it is also interesting to note that, in these 1,3-disubstituted allylic substrates, the thermal 1,3-sigmatropic shift should have the *antara* preference, normally not observed for steric reasons [9]. It was previously shown that substituted allylic and vinylic phosphonates can easily isomerize into each other via a prototropic process in the ROH/RO$^-$ system [10]. In the case of the unsubstituted allylphosphonate $H_2C=CHCH_2$-PO_3Et_2, however, it was demonstrated that, after quantitative isomerization to the 1-propenylphosphonate, a Michael-type addition of EtO$^-$ had followed at the β position. Therefore, not unexpectedly, alkoxy bases reacted with silanyl-propenylphosphonates **1** according to the addition pattern. In ethanol, **1a** reacted with NaOEt giving, in good yields exclusively the adduct $Me_3SiCH_2CH(OEt)CH_2PO_3Et_2$ (**4**); with NaOMe in methanol transesterification took place besides the addition, yielding the corresponding dimethyl ester of the 2-methoxy adduct, $Me_3SiCH_2CH(OMe)CH_2PO_3Me_2$. These results obviously indicate that the deprotonation in the γ position (with respect to the P atom) is much slower than the addition of a base. In fact, treatment of **1a,b** with BuLi (or ^{t}BuLi), followed by quenching with ammonium chloride, led to the isomerization products **2** and **3** as minor products, but the base-added compounds, (**5a,b**, **6a,b**) were still the major products (Scheme 4).

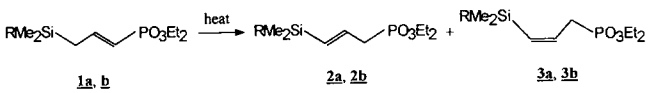
The final yield of **5(6)** could be also increased by multiple treatment of **1** with ^{t}BuLi. For example, **1a** was treated with an excess of ^{t}BuLi and the ratio of the addition vs. isomerization product (as well as the parent compound) was determined by ^{31}P NMR spectroscopy as shown in Table 1.

In consequence, lithiation of substrates **1** by means of alkyllithium proved impractical because of the inherent participation of the addition of the reagent across the olefinic bond. Competition from the addition reaction could be minimized when lithium diisopropylamide (LDA) was used as the deprotonating agent. Under conditions identical to those applied for treatment with BuLi, **1a**, **1b** could be converted by LDA to **2** or **3** with 70% yield, and with less than 5% of the addition product formed. When **1b** was treated with LDA, followed by a haloalkane (MeI or $PhCH_2Br$), the corresponding C-alkylated products were obtained, giving evidence for the effective deprotonation of the substrates by LDA. Alkylation



1 a, R= Me
b, R= ^{t}Bu

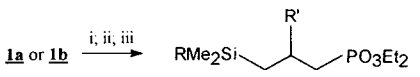
SCHEMA 2



1a, b 2a, 2b 3a, 3b

a, R= Me
b, R= ^{t}Bu

SCHEMA 3



i: R'Li; ii: $NH_4Cl_{(aq)}$ at -78°C; iii: rt **5a** (R= Me, R'= n-Bu) **6a** (R= ^{t}Bu, R'= n-Bu)
5b (R= Me, R'= ^{t}Bu) **6b** (R= ^{t}Bu, R'= ^{t}Bu)

SCHEMA 4

TABLE 1 Composition of the Reaction Product of **1a** with ^{t}BuLi Determined by ^{31}P NMR Spectroscopy

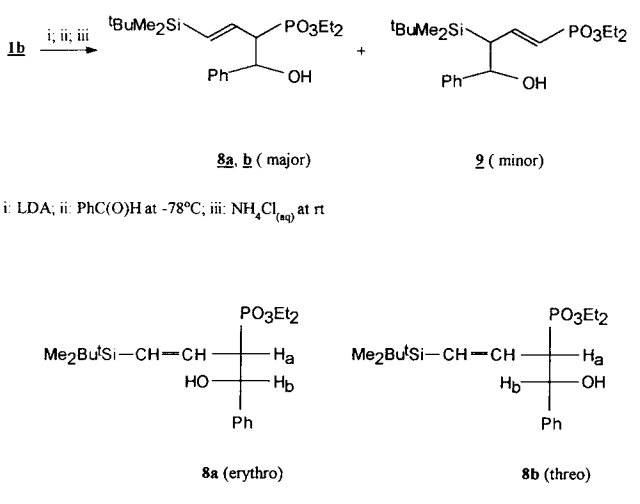
Number of Treatments with ^{t}BuLi	*Proportions of Compounds (%)*		
	5b	***2a/b***	***1***
1	50.0	40.1	9.9
2	54.1	42.3	3.6
3	57.1	41.7	1.2
4	63.5	36.7	1.0

occurred exclusively at the α carbon of **1b**, yielding the α-substituted silanylallylphosphonates, **7**, $Me_2{}^tBuSiCH{=}CH{-}CH(R){-}PO_3Et_2$ (**7a**, R = Me; **7b**, R = $PhCH_2$), stable compounds that could be purified by distillation.

With regard to the Wittig–Horner reaction, the reaction of silanylphosphonate **1b** with aldehydes was studied next in order to establish the potential of the product as a precursor in diene formation. The earlier results [11,12] demonstrated that the addition of lithiated allylphosphonate to aldehydes is not very regioselective, often leading to some formation of the thermodynamically controlled γ adduct. Silanylpropenylphosphonate **1b** showed similar behavior: after deprotonation with LDA, the reaction with benzaldehyde yielded the α adduct **8** (as a pair of diastereomers), together with a minor amount of the γ adduct **9** (Scheme 5).

Purification of the product was first carried out by bulb to bulb distillation, which allowed us to separate the adducts from nonvolatile impurities. Subsequent multiple column chromatography (CH_2Cl_2 EtOAc, 3:1) led to the isolation of **9**, as well as the main product **8**, isolated as a mixture of diastereomers (**8a**, **8b**). Both regioisomers could be unambiguously identified by NMR (^{31}P, ^1H, ^{13}C) spectroscopy. The remarkable property of adducts **8** and **9** was their thermal stability; during the distillation of the crude product at 180°C, no signs of decomposition could be observed. In the case of **1a** as a starting material, the adducts analogous to **9** and **8** (also a pair of diastereomers, δ_p 28.10, 27.97) could be identified by NMR spectroscopy. The attempts to purify those trimethylsilyl derivatives always led to extensive decomposition.

It can be concluded that the silanylpropenylphosphonates **1** represent vinylic phosphonates, for which a nucleophilic addition to the β carbon is favored over the deprotonation at the γ carbon. The reason for this behavior may be the decrease of the acidity of the γ-hydrogen atom as a result of the presence of the trialkylsilyl substituent. In agreement with that conclusion, when the isomeric system was used as a starting material (**2b/3b** instead of **1b**) in the reaction with benzaldehyde, a significant (25%) increase in the yield of the addition product was obtained. Since it was observed that the bulkiness of the trialkylsilyl substituent (Me_3Si vs. $Me_2{}^tBuSi$) had a considerable effect on the chemical behavior of the silanylpropenylphosphonate system, further studies on the chemistry of those derivatives carrying variable $R_2R'Si$ substituents are currently being carried out in our laboratory.



SCHEME 5

EXPERIMENTAL

Solvents and commercially available substrates were purified by conventional methods immediately before use. All reactions were carried out in an atmosphere of dry nitrogen. NMR spectra were recorded as solutions in $CDCl_3$ on a Bruker AC 300 spectrometer. Chemical shifts are given in ppm relative to $SiMe_4$ (^1H, ^{13}C) as an internal standard, and 85% H_3PO_4 (^{31}P) as an external standard. Proton-coupled ^{13}C-NMR spectra are given. Mass spectra were recorded on a Varian MAT-212 double-focusing direct-inlet spectrometer and GC-coupled spectrometer at an ionization potential of 70 eV. For column chromatography, Merck Kieselgel 60 (0.063–0.200 mm) was used.

Allyl-phosphonic Acid Diethyl Ester

It was prepared from triethyl phosphite and allyl bromide [13]. Colorless liquid, b.p. 54°C (0.2 Torr), yield 94%. ^1H-NMR, δ_H: 1.20 (6H, t, J_{HH} = 7.11 Hz, 2× Me of OEt), 2.51 (2H, d of d, J_{HH} = 7.20 Hz, J_{HP} = 21.92 Hz, α-CH_2), 4.00 (4H, quint, J_{HH} = J_{HP} = 7.00 Hz, 2× CH_2 of OEt), 5.11 (2H, m, $J_{HH(trans)}$ = 16.9 Hz, $J_{HH(cis)}$ = 6.9 Hz, $J_{HH(gem)}$ = 1.2 Hz, γ-CH_2), 5.71 (1H, m, β-CH); ^{13}C-NMR, δ_C: 15.96 (dq, J_{CP} = 5.96 Hz, J_{CH} = 142.04 Hz, 2× Me of OEt), 31.34 (dt, J_{CP} = 139.47 Hz, J_{CH} = 127.32 Hz, α-CH_2), 61.40 (dt, J_{CP} = 6.49 Hz, J_{CH} = 147.32 Hz, 2× CH_2 of OEt), 119.34 (dt, J_{CP} = 14.41 Hz, J_{CH} = 154.72 Hz, γ-CH_2), 127.13 (dd, J_{CP} = 11.17 Hz, J_{CH} = 159.02 Hz, β-CH); ^{31}P-NMR, δ_P: 27.5; MS: 178 (M^+, 5%), 109 (Et-OPO_2H^+, 100%).

General Procedure for the Preparation of Silanyl-propenyl Phosphonate Esters

n-Butyllithum (1.6 M solution in hexane, 1.2 mol equiv.), or tert-butyllithium (1.7 M solution in pentane, 1.1 mol equiv.), or lithium diisopropylamide (10% suspension in pentane, 1.3 mol equiv.) was cooled to −78°C. A solution of the allylphosphonate in THF (1 mol equiv.) was added at −78°C and stirred at this temperature for 60–90 minutes. The electrophile (1.2 mol equiv.) was then added drop-

wise to the solution. After having been stirred for an additional 30–45 minutes at −78°C, the reaction mixture was allowed to warm to room temperature and the reaction was quenched by addition of 10% aq. ammonium chloride, and the product was extracted with ether. The combined ether fraction was dried with magnesium sulfate, evaporated under reduced pressure, and purified by bulb to bulb distillation.

3-(Trimethylsilanyl)-propenyl-phosphonic Acid Diethyl Ester, **1a**

Colorless liquid, 130°C (0.2 Torr) (bulb to bulb), yield: 70%. ^{1}H-NMR, δ_H: −0.02 (9H, s, 3× Me of Me_3Si), 1.24 (6H, t, J_{HH} = 7.03 Hz, 2× Me of OEt), 1.70 (2H, d, J_{HH} = 8.64 Hz, γ-CH_2), 3.98 (4H, quint, J_{HH} = J_{HP} = 7.08 Hz, 2× CH_2 of OEt), 5.35 (1H, m, α-CH), 6.72 (1H, m, β-CH); ^{13}C-NMR, δ_C: −1.91 (q, J_{CH} = 104.22 Hz, Me of Me_3Si), 16.35 (dq, J_{CP} = 6.49 Hz, J_{CH} = 127.47 Hz, 2× Me of OEt), 27.00 (dt, J_{CP} = 21.28 Hz, J_{CH} = 124.37 Hz, γ-CH_2), 61.32 (dt, J_{CP} = 4.98 Hz, J_{CH} = 142.79 Hz, 2× CH_2 of OEt), 114.08 (dd, J_{CP} = 191.69 Hz, J_{CH} = 147.46 Hz, α-CH), 152.09 (dd, J_{CP} = 5.21 Hz, J_{CH} = 149.73 Hz, β-CH); ^{31}P-NMR, δ_P: 20.04; MS: 250 (M^+, 10%), 235 (M^+-Me, 11%), 205 (M^+-OEt, 7%), 137 ($PO_3Et_2^+$, 22%), 92 (PO_2Et^+, 96%), 73 (Me_3Si^+, 100%).

3-(tert-Butyldimethylsilanyl)-propenyl-phosphonic Acid Diethyl Ester, **1b**

Colorless liquid, 160°C (0.2 Torr) (bulb to bulb), yield: 61%. ^{1}H-NMR, δ_H: −0.05 (6H, s, 2× Me of Me_2Si), 0.85 (9H, s, 3× Me of ^{t}BuSi), 1.27 (6H, t, J_{HH} = 7.08 Hz, 2× Me of OEt), 1.74 (2H, d, J_{HH} = 8.40 Hz, γ-CH_2), 3.99 (4H, quint, J_{HH} = J_{HP} = 7.09 Hz, 2× CH_2 of OEt), 5.39 (1H, m, α-CH), 6.76 (1H, m, β-CH); ^{13}C-NMR, δ_C: −6.43 (q, J_{CH} = 117.34 Hz, Me of Me_2Si), 16.33 (dq, J_{CP} = 6.41 Hz, J_{CH} = 126.85 Hz, 2× Me of OEt), 23.05 (dt, J_{CP} = 22.11 Hz, J_{CH} = 124.59 Hz, γ-CH_2), 26.37 (q, J_{CH} = 119.23 Hz, Me of ^{t}BuSi), 32.65 (s, C of ^{t}BuSi), 61.32 (dt, J_{CP} = 5.00 Hz, J_{CH} = 146.47 Hz, 2× CH_2 of OEt), 114.21 (dd, J_{CP} = 189.70 Hz, J_{CH} = 155.76 Hz, α-CH), 152.53 (dd, J_{CP} = 5.70 Hz, J_{CH} = 155.15 Hz, β-CH); ^{31}P-NMR, δ_P: 19.96; MS: 292 (M^+, 4%), 277 (M^+-Me, 8%), 235 (M^+-Bu, 19%), 220 (M^+-Bu-Me, 29%), 177 (M^+-$Me_2{}^t$BuSi, 90%), 153 ($C_9H_{17}Si^+$, 95%).

Prototopic Isomerization of Phosphonates **1a** *and* **1b**

A mixture of lithium diisopropylamide (10% suspension in pentane, 1.4 mol equiv.) and THF was cooled to −78°C. A solution of the trialkylsilylpropenylphosphonate in THF was added slowly at the same temperature. After 45 minutes of stirring, the reaction was quenched by addition of 10% aq. ammonium chloride, and, after 15 minutes, the mixture was allowed to warm to room temperature with continuous stirring. The product was extracted with ether, and the combined ether fraction was worked up in the conventional way.

(E)-3-(Trimethylsilanyl)-allyl-phosphonic Acid Diethyl Ester, **2a**

Colorless liquid, 130°C (0.2 Torr) (bulb to bulb), yield: 81%. ^{1}H-NMR, δ_H: 0.02 (9H, s, 3× Me of Me_3Si), 1.24 (6H, t, J_{HH} = 7.01 Hz, 2× Me of OEt), 2.58 (2H, d, J_{HH} = 6.78 Hz, J_{HP} = 21.62 Hz, α-CH_2), 4.04 (4H, quint, J_{HH} = J_{HP} = 6.99 Hz, 2× CH_2 of OEt), 5.17 (1H, m, γ-CH), 5.89 (1H, m, β-CH); ^{13}C-NMR, δ_C: −1.49 (q, J_{CH} = 119.00 Hz, Me of Me_3Si), 16.34 (dq, J_{CP} = 6.11 Hz, J_{CH} = 126.32 Hz, 2× Me of OEt), 34.64 (dt, J_{CP} = 136.44 Hz, J_{CH} = 135.38 Hz, α-CH_2), 61.82 (dt, J_{CP} = 6.49 Hz, J_{CH} = 142.78 Hz, 2× CH_2 of OEt), 134.45 (dd, J_{CP} = 11.17 Hz, J_{CH} = 153.95 Hz, γ-CH), 136.88 (dd, J_{CP} = 11.77 Hz, J_{CH} = 146.02 Hz, β-CH); ^{31}P-NMR, δ_P: 27.34; MS: 250 (M^+, 7%), 235 (M^+-Me, 31%), 179 ($C_7H_{16}O_3P^+$, 98%), 137 ($PO_3Et_2^+$, 25%), 122 ($PO_3CH_2Et^+$, 97%), 73 (Me_3Si^+, 100%).

(E)-3-(tert-Butyldimethylsilanyl)-allyl-phosphonic Acid Diethyl Ester, **2b**

Colorless liquid, 160°C (0.2 Torr) (bulb to bulb), yield: 90%: ^{1}H-NMR, δ_H: −0.01 (6H, s, 2× Me of Me_2Si), 0.84 (9H, s, 3× Me of ^{t}BuSi), 1.27 (6H, t, J_{HH} = 6.96 Hz, 2× Me of OEt), 2.67 (2H, d, J_{HH} = 6.64 Hz, J_{HP} = 21.88 Hz, α-CH_2), 4.04 (4H, quint, J_{HH} = J_{HP} = 7.37 Hz, 2× CH_2 of OEt), 5.41 (1H, m, γ-CH), 5.20 (1H, m, β-CH); ^{13}C-NMR, δ_C: −6.26 (q, J_{CH} = 119.70 Hz, Me of Me_2Si), 16.41 (dq, J_{CP} = 6.11 Hz, J_{CH} = 126.79 Hz, 2× Me of OEt), 26.32 (q, J_{CH} = 124.76 Hz, 3× Me of ^{t}BuSi), 29.97 (s, C of ^{t}BuSi), 34.82 (dt, J_{CP} = 136.38 Hz, J_{CH} = 131.32 Hz, α-CH_2), 61.80 (dt, J_{CP} = 6.57 Hz, J_{CH} = 145.66 Hz, 2× CH_2 of OEt), 134.04 (dd, J_{CP} = 12.60 Hz, J_{CH} = 144.08 Hz, γ-CH), 135.85 (dd, J_{CP} = 11.25 Hz, J_{CH} = 150.26 Hz, β-CH); ^{31}P-NMR, δ_P: 27.32; MS: 277 (M^+-Me, 6%), 235 (M^+-Bu, 51%), 179 ($C_7H_{14}O_3P^+$, 100%), 153 ($C_9H_{17}Si^+$, 25%).

Reaction of Phosphonate **1a** *with Alkoxide Base*

1a (0.5 g) was dissolved in a 2.2 mol solution of sodium alkoxide in the corresponding alcohol and the solution was incubated at 25°C for 20 hours; 10% aq. ammonium chloride was added until the pH was approximately 7, and the product was extracted with ether and worked up in the conventional way.

2-Ethoxy-3-(trimethylsilanyl)-propyl-phosphonic Acid Diethyl Ester, **4**

^{31}P-NMR, δ_P: 29.44, or 2-methoxy-3-(trimethylsilanyl)-propyl-phosphonic acid dimethyl ester, ^{31}P-NMR, δ_P: 30.34.

Reaction of Phosphonates **1a** *and* **1b** *with Alkyllithium*

The same procedure was used as described previously, but instead of LDA, butyllithium (1.6 M solution in hexane, 1.2 mol equiv.) or *tert*-butyllithium (1.7 M solution in pentane, 1.1 mol equiv.) was used.

2-Trimethylsilanylmethyl-hexanyl-phosphonic acid Diethyl Ester, **5a**

^{31}P-NMR, δ_P: 32.44; MS: 308 (M^+, 7%), 279 (M^+-Et, 8%), 265 (M^+-Et-Me, 29%), 251 (M^+-Bu, 23%), 137 ($PO_3Et_2^+$, 28%), 73 (Me_3Si^+, 100%).

2-(Trimethylsilanyl-methyl)-3,3-dimethylbutyl-phosphonic Acid Diethyl Ester, **5b**

^{31}P-NMR, δ_P: 33.96; MS: 293 (M^+-Me, 34%), 265 (M^+-Et-Me, 16%), 251 (M^+-Bu, 34%), 137 ($PO_3Et_2^+$, 18%), 73 (Me_3Si^+, 100%)

2-[(tert-Butyldimethylsilanyl)methyl]-hexanyl-phosphonic Acid Diethyl Ester, **6a**

^{31}P-NMR, δ_P: 32.72; MS: 350 (M^+, 2%), 335 (M^+-Me, 6%), 293 (M^+-Bu, 100%), 265 (M^+-Bu-Et, 30%), 236 (M^+-2Bu, 82%), 222 (M^+-2Bu-Me, 26%), 137 ($PO_3Et_2^+$, 12%).

2[(tert-Butyldimethylsilanyl)-methyl]-3,3-dimethylbutyl-phosphonic Acid Diethyl Ester, **6b**

^{31}P-NMR, δ_P: 33.73; MS: 335 (M^+-Me, 9%), 293 (M^+-Bu, 100%), 236 (M^+-2Bu, 69%), 222 (M^+-2Bu-Me, 35%), 179 (M^+-BuMe$_2$Si, 41%), 137 ($PO_3Et_2^+$, 17%).

Alkylation of Phosphonate **1b**

A mixture of lithium diisopropylamide (10% suspension in pentane, 1.3 mol equiv.) and THF was cooled to −78°C. A solution of **1b** in THF was added slowly at the same temperature. After 90 minutes of stirring, the electrophile (1.2 mol equiv.) in THF was added, and after 25 minutes the solution was warmed to room temperature. The reaction was quenched with 10% aq. ammonium chloride, the product was extracted with ether, and the combined ether fraction was worked up in the conventional way.

(E)-3-(tert-Butyldimethylsilanyl)-1-methyl-allyl-phosphonic Acid Diethyl Ester, **7a**

Colorless liquid, b.p.: 145°C (0.2 Torr) (bulb to bulb), yield: 59%: ^{1}H-NMR, δ_H: −0.01 (6H, s, 2× Me of Me$_2$Si), 0.83 (9H, 3× Me of ^{t}BuSi), 1.27 (3H, d, J_{HH} = 6.86 Hz, Me of C(1)-Me), 1.29 (6H, t, J_{HH} = 7.04 Hz, 2× Me of OEt), 2.65 (1H, m, α-CH), 4.05 (4H, q, $J_{HH} = J_{HP}$ = 7.17, 2× CH_2 of OEt), 5.80 (1H, d of d, J_{HH} = 18.70 Hz, J_{HH} = 4.40 Hz, γ-CH), 6.00 (1H, m, β-CH); ^{13}C-NMR, δ_C: −6.20 (q, J_{CH} = 119.30 Hz, Me of Me$_2$Si), 13.30 (dq, J_{CP} = 5.96 Hz, J_{CH} = 129.20 Hz, Me of C(1)-Me), 16.44 (dq, J_{CP} = 5.66 Hz, J_{CH} = 126.30 Hz, 2× Me of OEt), 26.34 (q, J_{CH} = 124.76 Hz, 3× Me of ^{t}BuSi), 28.42 (s, C of ^{t}BuSi), 39.09 (dt, J_{CP} = 136.68 Hz, J_{CH} = 132.1 Hz, α-CH_2), 61.86 (dt, J_{CP} = 7.62 Hz, J_{CH} = 149.20 Hz, 2× CH_2 of OEt), 130.24 (dd, J_{CP} = 11.32 Hz, J_{CH} = 141.19 Hz, γ-CH), 142.94 (dd, J_{CP} = 9.36 Hz, J_{CH} = 139.80 Hz, β-CH); ^{31}P-NMR, δ_P: 30.29; MS: 306 (M^+, 3%), 291 (M^+-Me, 4%), 263 (18%), 249 (M^+-Bu, 45%), 234 (M^+-Bu-Me, 6%), 220 (M^+-Bu-Et, 22%), 193 ($C_8H_{18}O_3P$, 100%), 139 ($PO_3Et_2H_2^+$, 26%), 121 ($PO_2Et_2^+$, 50%).

(E)-1-Benzyl-3-(tert-butyldimethylsilanyl)-allyl-phosphonic Acid Diethyl Ester, **7b**

Colorless liquid, b.p.: 165°C (0.2 Torr) (bulb to bulb), purification by column chromatography (CH_2Cl_2/ethyl acetate, 3:1), yield: 71%: ^{1}H-NMR, δ_H: −0.11 (3H, s, Me^a of Me$_2$Si), −0.09 (3H, s, Me^b of Me$_2$Si), 0.70 (9H, 3× Me of ^{t}BuSi), 1.26 (3H, t, J_{HH} = 7.01 Hz, Me^a of OEt), 1.28 (3H, t, J_{HH} = 7.06 Hz, Me^b of OEt), 2.81 (2H, m, CH_2 of benzyl), 3.18 (1H, m, α-CH), 4.06 (4H, d of q, $J_{HH} = J_{HP}$ = 7.13, 2× CH_2 of OEt), 5.56 (1H, d of d, J_{HH} = 18.63 Hz, J_{HH} = 4.62 Hz, γ-CH), 5.80 (1H, m, β-CH), 7.1 (5H, m, Ph); ^{13}C-NMR, δ_C: −6.43 (q, J_{CH} = 120.00 Hz, Me^a of Me$_2$Si), −6.22 (q, J_{CH} = 119.32 Hz, Me^b of Me$_2$Si), 16.39 (dq, J_{CP} = 6.41 Hz, J_{CH} = 126.86 Hz, 2× Me of OEt), 26.28 (q, J_{CH} = 124.83 Hz, 3× Me of ^{t}BuSi), 31.16 (s, C of ^{t}BuSi), 34.53 (dt, J_{CP} = 3.92 Hz, J_{CH} = 130.07 Hz, CH_2 of benzyl), 47.74 (dt, J_{CP} = 134.64 Hz, J_{CH} = 129.66 Hz, α-CH_2), 61.75 (dt, J_{CP} = 7.32 Hz, J_{CH} = 144.67 Hz, CH_2^a of OEt), 62.21 (dt, J_{CP} = 6.79 Hz, J_{CH} = 147.99 Hz, CH_2^b of OEt), 126.10 (d, J_{CH} = 161.58 Hz, p-CH), 128.12 (d, J_{CH} = 159.16 Hz, o-CH), 129.02 (d, J_{CH} = 156.97 Hz, m-CH), 133.80 (dd, J_{CP} = 11.40 Hz, J_{CH} = 130.49 Hz, γ-CH), 138.70 (s, C_1-Ph), 140.66 (dd, J_{CP} = 9.06 Hz, J_{CH} = 149.50 Hz, β-CH); ^{31}P-NMR, δ_P: 28.65; MS: 367 (M^+-Me, 2%), 325 (M^+-Bu, 19%), 139 ($PO_3Et_2H_2^+$, 40%), 121 ($PO_2Et_2^+$, 43%), 91 ($PhCH_2^+$, 100%), 77 (Ph^+, 22%).

Erythro-3-(tert-Butyldimethylsilanyl)-1-hydroxylphenylmethyl-allyl-phosphonic Acid Diethyl Ester, **8a**

^{1}H-NMR, δ_H: −0.09 (3H, s, Me^a of Me$_2$Si), −0.06 (3H, s, Me^b of Me$_2$Si), 0.71 (9H, 3× Me of ^{t}BuSi), 1.30 (3H, t, J_{HH} = 7.00 Hz, Me^a of OEt), 1.31 (3H, t, J_{HH} = 6.91 Hz, Me^b of OEt), 2.82 (1H, d of d of d, J_{HP} = 17.40 Hz, $J_{HH(allylic)} = J_{HH(vic)}$ = 9.11 Hz, α-CH), 4.13 (2H, quint, $J_{HH} = J_{HP}$ = 7.04 Hz, CH_2^a of OEt), 4.14 (2H, quint, $J_{HH} = J_{HP}$ = 7.11 Hz, CH_2^b of OEt), 4.67 (1H, s, OH), 5.26 (1H, d of t, J_{HH} = 9.49 Hz, J_{HH} = 2.30 Hz, γ-CH), 5.51 (1H, d of d, J_{HH} = 9.32 Hz, J_{HP} = 4.12 Hz, CH of benzyl), 6.06 (1H, d of d of d, $J_{HH(trans)}$ = 18.65 Hz, $J_{HH(vic)}$ = 9.53 Hz, J_{HP} = 5.60 Hz,

β-CH), 7.22 (5H, m, Ph); ^{13}C-NMR, δ_C: −6.44 (q, J_{CH} = 119.54 Hz, Me^a of Me_2Si), −6.19 (q, J_{CH} = 119.24 Hz, Me^b of Me_2Si), 16.32 (dq, J_{CP} = 5.50 Hz, J_{CH} = 127.39 Hz, 2× Me of OEt), 26.11 (q, J_{CH} = 123.58 Hz, 3× Me of ^{t}BuSi), 29.92 (s, C of ^{t}BuSi), 54.14 (dt, J_{CP} = 131.55 Hz, J_{CH} = 128.90 Hz, α-CH_2), 61.87 (dt, J_{CP} = 6.84 Hz, J_{CH} = 147.63 Hz, CH_2^a of OEt), 62.90 (dt, J_{CP} = 7.11 Hz, J_{CH} = 146.92 Hz, CH_2^b of OEt), 71.88 (dd, J_{CP} = 4.53 Hz, J_{CH} = 146.94 Hz, CH of benzyl), 126.00 (d, o-CH), 127.18 (d, p-CH), 127.91 (d, m-CH), 136.16 (dd, J_{CP} = 7.62 Hz, J_{CH} = 124.30 Hz, γ-CH), 136.64 (dd, J_{CP} = 11.32 Hz, J_{CH} = 145.13 Hz, β-CH), 141.13 (s, C_1 of Ph); ^{31}P-NMR, δ_P: 28.65.

Threo-3-(tert-Butyldimethylsilanyl)-1-hydroxylphenylmethyl-allyl-phosphonic Acid Diethyl Ester, **8b**

^{1}H-NMR, δ_H: −0.20 (3H, s, Me^a of Me_2Si), −0.14 (3H, s, Me^b of Me_2Si), 0.65 (9H, Me of ^{t}BuSi), 1.22 (3H, t, J_{HH} = 7.03 Hz, Me^a of OEt), 1.23 (3H, t, J_{HH} = 7.05 Hz, Me^b of OEt), 2.91 (1H, d of d of d, J_{HP} = 21.80 Hz, $J_{HH(allylic)}$ = 9.53 Hz, $J_{HH(vic)}$ = 2.32 Hz, α-CH), 4.03 (2H, quint, J_{HH} = J_{HP} = 7.00 Hz, CH_2^a of OEt), 4.04 (2H, quint, J_{HH} = J_{HP} = 7.01 Hz, CH_2^b of OEt), 4.66 (1H, s, OH), 4.92 (1H, d of d of d, J_{HH} = 11.39 Hz, J_{HH} = 9.13 Hz, J_{HH} = 2.17 Hz, γ-CH), 5.44 (1H, d of d, J_{HH} = 9.25 Hz, J_{HH} = 3.82 Hz, CH of benzyl), 5.58 (1H, d of d of d, $J_{HH(trans)}$ = 18.50 Hz, $J_{HH(vic)}$ = 9.03 Hz, J_{HP} = 4.76 Hz, β-CH), 7.23 (5H, m, Ph); ^{13}C-NMR, δ_C: −6.61 (q, J_{CH} = 119.47 Hz, Me^a of Me_2Si), −6.49 (q, J_{CH} = 119.54 Hz, Me^b of Me_2Si), 16.24 (dt, J_{CP} = 6.12 Hz, J_{CH} = 127.39 Hz, 2× Me of OEt), 26.03 (q, J_{CH} = 125.13 Hz, 3× Me of ^{t}BuSi), 31.59 (s, C of ^{t}BuSi), 54.68 (dt, J_{CP} = 129.96 Hz, J_{CH} = 135.54 Hz, α-CH_2), 62.33 (dt, J_{CP} = 7.81 Hz, J_{CH} = 143.88 Hz, CH_2^a of OEt), 62.43 (dt, J_{CP} = 7.63 Hz, J_{CH} = 143.88 Hz, CH_2^b of OEt), 73.27 (dt, J_{CP} = 4.53 Hz, J_{CH} = 146.64 Hz, CH_2 of benzyl), 126.00 (d, o-CH), 126.89 (d, p-CH), 128.14 (d, m-CH), 134.36 (dd, J_{CP} = 10.19 Hz, J_{CH} = 121.73 Hz, γ-CH), 138.20 (dd, J_{CP} = 10.04 Hz, J_{CH} = 148.07 Hz, β-CH), 141.34 (s, C_1 of Ph); ^{31}P-NMR, δ_P: 28.25; MS of both stereoisomers: 383 (M^+-Me, 2%), 341 (M^+-Bu, 4%), 323 (M^+-Bu-H_2O, 5%), 235 ($MeSiC_3H_3PO_3Et_2^+$, 32%), 220 ($Me_2SiC_3H_3PO_3Et^+$, 11%), 178 ($C_3H_5PO_3Et_2^+$, 100%), 121 ($PO_2Et_2^+$, 21%), 106 (PhCHO, 45%), 77 (Ph^+, 58%).

3-(tert-Butyldimethylsilanyl)-4-hydroxy-4-phenyl-but-1-enyl-phosphonic Acid Diethyl Ester, **9**

^{1}H-NMR, δ_H: 0.03 (3H, s, Me^a of Me_2Si), 0.07 (3H, s, Me^b of Me_2Si), 0.89 (9H, s, 3× Me of ^{t}BuSi), 1.04 (6H, t, J_{HH} = 7.13 Hz, 2× Me of OEt), 1.77 (1H, m, γ-CH), 3.75 (4H, m, 2× CH_2 of OEt), 4.44 (1H, d, J_{HH} = 9.81 Hz, δ-CH), 5.70 (1H, d of d, J_{HH} = 18.55 Hz, J_{HP} = 25.90 Hz, α-CH), 6.66 (1H, m, β-CH), 7.28 (5H, m, Ph); ^{13}C-NMR, δ_C: 0.98 (q, J_{CH} = 117.89 Hz, 2× Me of Me_2Si), 16.35 (dq, J_{CP} = Hz, J_{CH} = 126.60 Hz, 2× Me of OEt), 17.90 (dt, J_{CP} = 16.91 Hz, J_{CH} = Hz, γ-CH_2), 26.27 (q, J_{CH} = 125.06 Hz, 3× Me of ^{t}BuSi), 31.13 (s, C of ^{t}BuSi), 61.92 (dt, J_{CP} = 5.05 Hz, J_{CH} = Hz, 2× CH_2 of OEt), 69.93 (dd, J_{CP} = 9.58 Hz, J_{CH} = 145.36 Hz, CH of benzyl), 117.31 (dt, J_{CP} = 137.97 Hz, J_{CH} = 129.66 Hz, α-CH_2), 125.78 (d, o-C of Ph), 127.02 (d, p-CH of Ph), 128.10 (d, m-CH), 139.70 (s, C_1 of Ph), 145.30 (dt, J_{CP} = 8.75 Hz, J_{CH} = 156.00 Hz, β-CH_2); ^{31}P-NMR, δ_P: 22.29; MS: 398 (M^+, 2%), 397 (M^+-H, 3%), 383 (M^+-Me, 3%), 382 (M^+-H-Me, 3%), 341 (M^+-Bu, 11%), 323 (M^+-Bu-H_2O, 20%), 295 (M^+-Bu-OEt-H, 13%), 267 (M^+-Et-OEt, 15%), 249 (19%), 129 ($PhC_4H_4^+$, 100%), 77 (Ph^+, 23%).

ACKNOWLEDGMENT

Financial support form the University of Pretoria and the Foundation for Research Development is gratefully acknowledged.

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