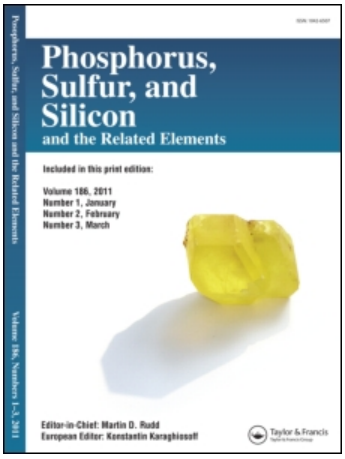

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A MODIFIED McCORMACK SYNTHESIS OF 3-SILYLATED PHOSPHOL-3-ENES

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A MODIFIED McCORMACK SYNTHESIS OF 3-SILYLATED PHOSPHOL-3-ENES

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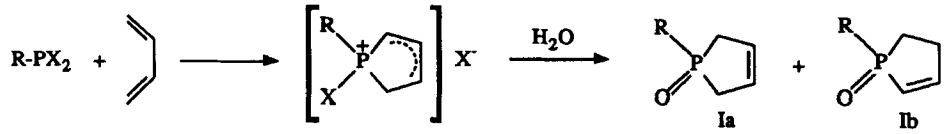
We report the synthesis of the first 3-silylated phosphol-3-enes using a modified McCormack reaction sequence. The complete protodesilylation observed in standard conditions is suppressed when the reaction between 2-silylated 1,3-butadiene and dichlorophenylphosphine is carried out in the presence of a small amount of copper stearate in acetic anhydride at 50°C. The new phospholenes contain a reactive vinylsilane function which has been epoxidized by *m*-chloroperbenzoic acid. The bicyclic compound has a *cis* structure as established by classical spectroscopic methods and corroborated by molecular modelling.

Key words: 3-Silylated phospholenes, 1-phenyl-3-trimethylsilyl-1-phosphol-3-ene-1-oxide, 3-phenyl-1-trimethylsilyl-6-oxa-3 phosphabicyclo[3.1.0]hexane 3-oxide, epoxidation.

INTRODUCTION

The synthesis of heterocycles containing one phosphorus atom was first reported by McCormack in 1953.[1] Application of the Diels Alder reaction which utilizes 1,3-dienes and trivalent phosphorus halides as dienophiles provided a wide range of new five-membered ring compounds:

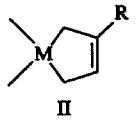


This reaction is depending on several parameters. K. Moedritzer[2] and L. D. Quin[3,4] have reported that the yields and nature of adducts depend mainly on the structure of phosphines, dienes, and also on reaction time, solvent and temperature of the reaction mixture.[5,6]

More recently, D. Price *et al.*[6] have shown that the McCormack reaction is obviously dependent on a number of different variables which are surely interactive rather than independent. So, an optimized procedure was applied for the synthesis of 1-methoxy-3-methyl-2-phospholene 1-oxide.

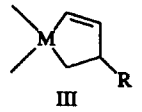
Another method to prepare phosphorus heterocycles, based on the addition of $[RPX_2 \cdot AlCl_3]$ to 1,4-dienes in which a double bond should migrate, was developed.[7]

In the course of our program, we have been interested in the synthesis and the chemical properties of a series of sila and germacyclopentenes such as (II) and



II

M = Si, Ge
R = H, Me

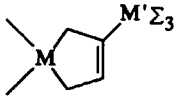


III

M = Si, Ge
R = H, $(CH_2)_2SiMe_3$, $(CH_2)_2SiCl_3$

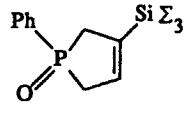
(III) for a long time. Such heterocompounds are useful synthons for the synthesis of, for example, polymeric materials[8a–d] and drugs.[8e–g]

Recently, we proposed an original synthesis of 3-silylated and 3-germylated sila and germacyclopentenes (IV).[9] Such derivatives have specific properties due to the carbon carbon double bond which is part of both an allylic and a vinylic system.



IV

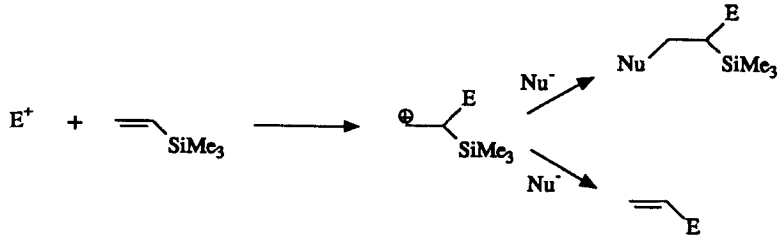
M = Si, Ge
M' = Si, Ge
Σ = Cl, Me, Ph



V

Σ = Me, Ph

It is known that vinylsilanes are particularly useful electrophilic reagents and intermediates in organic synthesis.[10] They react readily with a range of electrophiles to give E-substituted derivatives:



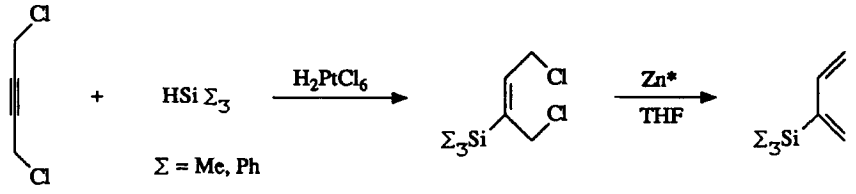
In this paper, we wish to describe the synthesis of 3-silylated phospholenes (V) using a McCormack reaction sequence. We will show the great importance of the silyl group on the synthesis of such phospholenes and will propose a modified McCormack reaction to prevent protodesilylation during the synthetic process.

RESULTS AND DISCUSSION

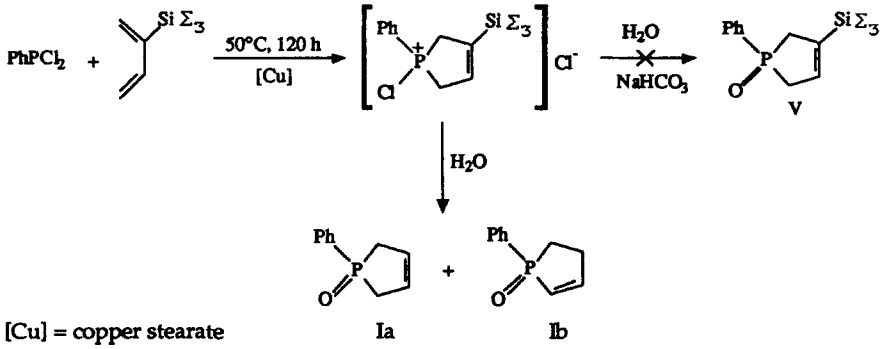
I. Synthesis of 3-silyl-1-phosphol-3-ene 1-oxides (V)

2-Silylated dienes are prepared as described in the literature.[9c,11] Catalytic hydrosilylation of commercially available 1,4-dichloro-2-butyne with different silanes in the presence of chloroplatinic acid produces quantitatively the *cis*-addition product

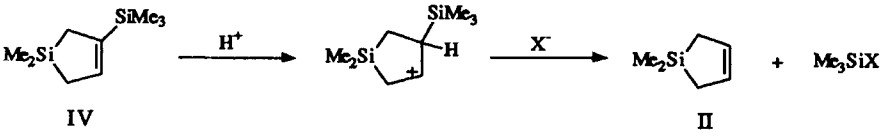
which can be reduced directly with excess zinc dust in refluxing THF:



We took into account the reaction sequence reported by Price *et al.*[6] and caused 2-silylated dienes to react with dichlorophosphine in the presence of copper stearate as an antioxidant at 50°C, during 120 hours. After treatment with an aqueous solution of hydrogenocarbonate, we only obtained a mixture of 1-phenyl-1-phosphol-3-ene 1-oxide (Ia) and 1-phenyl-1-phosphol-2-ene 1-oxide (Ib):



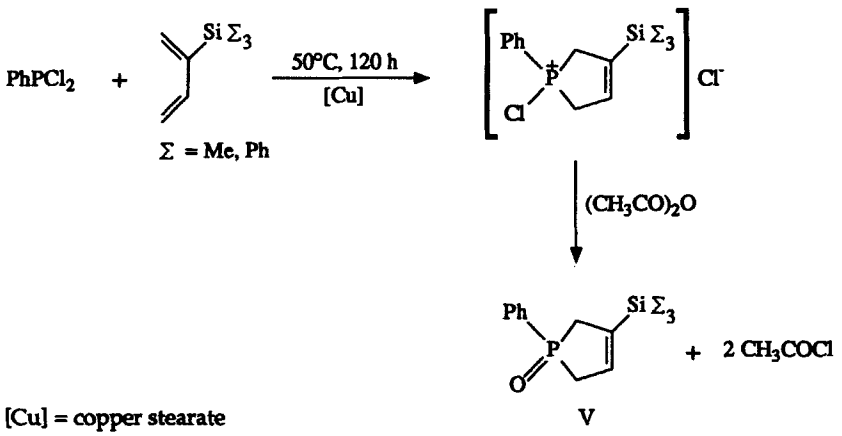
This result can be explained by the protodesilylation reaction of the vinylsilane intermediate (phosphonium salt) by HCl formed during the hydrolysis reaction. We also observed such a protodesilylation reaction in the silacyclopentene series (IV)[12]:



Therefore, this procedure is not useful for the preparation of silylated phospholenes such as (V).

In order to suppress the competing (or avoid) protodesilylation reaction, we attempted the reaction in acetic anhydride at 50°C, in the presence of copper stearate.

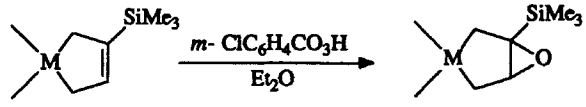
Synthesis of 3-silylated phospholenes (V) was achieved by this modified McCormack reaction sequence. However small amounts of (Ia) and (Ib) were still observed, probably due to a trace of protons formed during the easy hydrolysis of acetylchloride produced during the reaction.



Compounds (V) were isolated and purified by chromatography on silica gel using the mixture acetone/dichloromethane (90/10) as eluent.

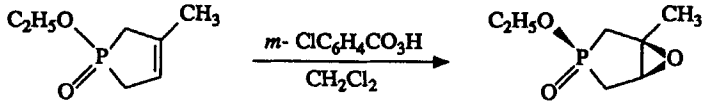
II. Synthesis and Structure of 6-oxa-1-trimethylsilyl-3-phenyl-3-phosphabicyclo[3.1.0]hexane 3-oxide (VIa)

We will verify that the oxidation of the carbon-carbon double bond of (V) with peracids does not induce protodesilylation. Such an epoxidation was performed in the sila and germacyclopentene series (IV). Protodesilylation was not observed and the corresponding epoxides were obtained in good yields.[12,13]



M = Si, Ge IV

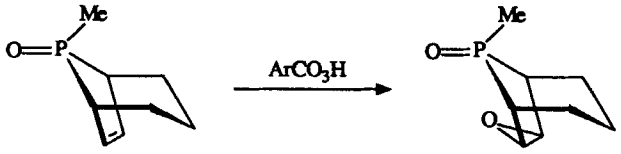
Epoxidation of the double bond of 3-phospholene derivatives was first reported in 1968 by Arbuzov *et al.*[14] Peracetic acid gave good yields of epoxides and the reactions were stereospecific, as shown below for example:



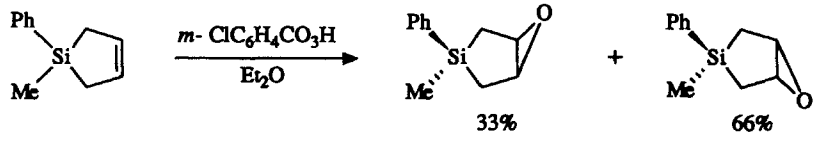
The formation of one stereoisomer was observed with several phospholenes. Dipole moment measurements[15] suggested that the unique isomer obtained resulted from a *trans* arrangement of the oxide ring and the phosphoryl group. These results were in agreement with those cited by other authors[16] relative to the direct oxidation of the double bond of phospholene derivatives with *m*-chloroperbenzoic acid. Epoxidation of the phospholene ring proceeds on the opposite side to the P=O bond. This observation can be assigned to the dipolar repulsions on approach of the reactants.[16]

The experimental dipole moment values of different epoxides of 3-phospholene 1-oxides measured by Arbuzov *et al.*[15] were around 3D. A comparison of experimental and calculated values proved a *trans* orientation of the ring epoxide and phosphoryl group.

Another approach proposed by Quin *et al.*,[16c] is based on the ^{13}C NMR spectroscopy studies, which also confirmed the structure of these products. However, this method was limited to 3-phospholene derivatives. When bicyclic 2-phospholene and 3-phospholene oxides are incorporated into a structure with an unusual steric constraint,[17] attack of the peracid occurs preferentially *syn* to the phosphoryl oxygen:

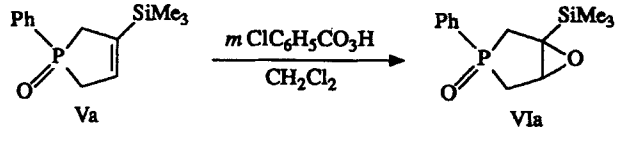


Such steric effects have also an important role in the orientation of the ring epoxide in the silacyclopentene series.[9a] In fact, substituents bonded to the silicon influence directly the isomeric ratio:



Keeping in mind all these results, we have prepared 6-oxa-1-trimethylsilyl-3-phenyl-3-phosphabicyclo[3.1.0]hexane 3-oxide (VI) from 3-trimethylsilyl-1-phosphol-3-ene 1-oxide (IIIa) and *m*-chloroperbenzoic acid in 52% yield.

The physical and chemical properties of this β-silylated α,β-epoxyphospholane were investigated in order to determine the structure of (VI):



Measurement of the dipole moment of epoxyphospholane (VI) reveals a value of 7.08D. This value is not in agreement with a *trans* disposition of the two oxygens but rather a *cis* one.

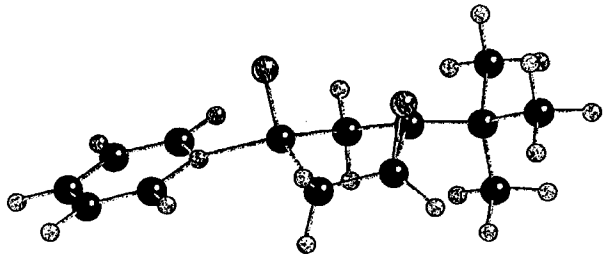
The presence of the trimethylsilyl group on the phosphacycle confers some specificity to the epoxide (VI). The high value of the dipole moment of (VI) encouraged us to investigate another way to resolve this conformational problem.

We performed a molecular modelling and applied the program MAD of Oxford Molecular/MM2 using the Newton Raphson Block Diagonal Minimiser. The calculated dipole moment is 5.34D for the conformer where the two oxygens of the ring epoxide and P=O are in *cis* position.

This conformation is favourable as the phenyl and trimethylsilyl groups are placed preferentially in a "pseudo" equatorial position.

All these results show that the epoxidation reaction is governed by several parameters. Influence of dipolar repulsions[15] appears easily dominated by other features of molecular geometry.

Additional examples relative to the structural effects on the steric pathway of oxidation of the carbon carbon double bond of β-silylated phosphacycles are needed to clarify the question of stereospecificity of this reaction. X-ray structures will be especially useful to confirm the structure of epoxides (VI).



CONCLUSION

We have shown that it is possible to prepare 3-silylated 3-phospholenes in a modified McCormack reaction. The presence of a silyl group has a significant influence on the reactivity and on the structure of the new silylated phosphacycles reported.

EXPERIMENTAL

^{1}H NMR spectra were obtained on a Bruker AC 80 and Bruker AM 300, Bruker AM 400 spectrometers operating in the Fourier transform mode. ^{13}C NMR spectra were run on a Bruker AC 200 with broad band proton decoupling. Ten percent solutions in chloroform-d_3 or benzene-d_6 were used to obtain NMR spectra. IR spectra were obtained on a Perkin Elmer 1600 FT instrument using samples in KBr pellets. GC/MS were obtained at an ionizing voltage of 70 eV on a Hewlett Packard 5890 mass spectrometer. A Hewlett Packard 5890 gas chromatograph was coupled to the mass spectrometer and was used as the MS inlet.

A Reichert-Thermovar apparatus was used for the determination of the melting points.

Elemental analyses were performed at the Ecole Nationale Supérieure de Chimie de Toulouse.

The dipole moments were measured in benzene at 25°C and calculated according to the Halverstadt-Kumler method. The dielectric permeabilities of the solutions were determined on a dipolmeter WTW, type DMO 1 and the densities on a Picnometer ASTM.

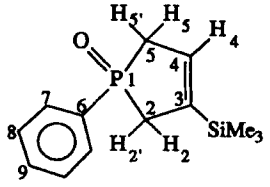
All glassware was dried overnight in an oven at 120°C. The apparatus was assembled and was then flame-dried whilst being swept with argon. All reactions were conducted under purified argon. Dichlorophenylphosphine and acetic anhydride were distilled immediately before use.

Synthesis of 1-phenyl-3-trimethylsilyl-1-phosphol-3-ene 1-oxide (Va)

2-Trimethylsilyl-1,3-butadiene (1.94 g, 15 mmoles) and copper stearate (0.04 g, 10 mol%) were placed in a two-necked round-bottomed flask equipped with a Teflon-covered magnetic stirring bar and a reflux condenser which was topped with a calcium chloride drying tube. Dichlorophenylphosphine (2.1 ml, 15 mmoles) and acetic anhydride (1.5 g, 15 mmoles) were successively introduced via a syringe. The reaction mixture was heated at 50°C for a period of 120 hours. Acetyl chloride, the excess of diene and acetic anhydride were removed by evaporation under reduced pressure. The crude product was purified by column chromatography on silica gel using the mixture acetone/dichloromethane (90/10) as

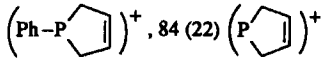
eluent. 0.84 g of pure product was obtained as a thick yellow oil. (R_F = 0.77). Yield. 22%. Anal. found: C, 60.73; H, 7.66. $C_{13}H_{19}OSiP$ (250.36). Calc.: C, 60.37; H, 7.64%.

^{31}P NMR δ: 54.68 (s).
IR: 3050, 3020, 2953, 2896, 1585 (C=C), 1437 (P—C_6H_5), 1397, 1248 (Me_3Si), 1210, 1173, 1114, 1022, 839, 745, 711, 695, 565 cm^{-1}. ^1H NMR δ: 0.10 (s, 9H, $SiMe_3$), 2.70 (m, 4H, H^2, $H^{2'}$, H^5, $H^{5'}$), 6.19 (m, 1H, H^4), 7.49 (m, 5H, C_6H_5). ^{13}C NMR δ: −2.35 (Me_3Si), 36.47 (C^2, d, J = 70.66 Hz), 36.63 (C^5, d, J = 63.26 Hz), 128.75, (C^8, d, J = 11.11 Hz), 130.08 (C^7, d, J = 9.19 Hz), 131.65 (C^9, d, J = 2.02 Hz), 135.78 (C^6, d, J = 88.42 Hz), 136.15 (C^3, d, J = 15.66 Hz), 143.43 (C^4, d, J = 3.87 Hz).



(Va)

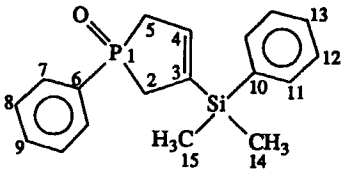
GCMS m/e (relative intensity): 250 (100) M^+, 235 (31) $(M—Me)^+$, 177 (20) $(M—Me_3Si)^+$ 162 (10)



73 (70) $(Me_3Si)^+$, 43 (57) $(MeSi)^+$.

Synthesis of 1-phenyl-3-phenyldimethylsilyl-1-phosphol-3-ene 1-oxide (Vb)

From 1 g (5.3 mmoles) of 2-phenyldimethyl-1,3-butadiene, 0.95 g (5.3 mmoles) of dichlorophenylphosphine and 0.54 g (5.3 mmoles) of acetic anhydride in the presence of 0.02 g (5 mol%) of copper stearate. Vb (0.36 g) was isolated as a clear, yellow liquid after purification by column chromatography on silica gel using the mixture acetone/dichloromethane (90/10) as eluent (R_F = 0.54). Yield. 21%.



(Vb)

RMN ^{31}P: 55.57 (s)
IR: 3432, 3050, 3019, 2955, 1585 (C=C), 1437 (P—C_6H_5), 1396, 1250 ($SiMe_3$), 1211, 1170, 1112, 1021, 833, 818, 778, 745, 713, 699 cm^{-1}. ^1H RMN δ: 0.314 (s, 6H, $SiMe_3$), 2.65 (m, 4H, H^2, $H^{2'}$, H^5, $H^{5'}$), 6.15 (m, 1H, H^4), 7.35 (m, 10H, Si—C_6H_5 and P—C_6H_5). ^{13}C RMN δ: −3.73 (C^{14}), −3.80 (C^{15}), 36.18 (C^2, d, J = 71.2 Hz), 36.4 (C^5, d, J = 63.83 Hz), 132.02 (C^9, d, J = 2.09 Hz), 142.17 (C^4, d, J = 4.33 Hz), 135.5 (C^6, d, J = 97.74 Hz). GSMS m/e (relative intensity): 312 (100) $(M)^+$, 297 (10) $(M—Me)^+$, 269 (1) $(M—SiMe_3)^+$, 135 (58) $(M—SiMe_2C_6H_5)^+$, 75 (34) $(Me_2SiOH)^+$, 43 (53) $(SiMe)^+$.

Synthesis of 3-phenyl-1-trimethylsilyl-6-oxa-3-phosphabicyclo[3.1.0]hexane 3-oxide (VIa)

1-Phenyl-3-trimethylsilyl-1-phosphol-3-ene 1-oxide (Va) (0.80 g, 3.35 mmoles) and 5 ml of dichloromethane were placed in a 50 ml two-necked round-bottomed flask equipped with a Teflon covered magnetic stirring bar and an efficient reflux condenser. 1.27 g (3.6 mmoles) of *m*-chloroperbenzoic acid in 9 ml of CH_2Cl_2 was added via a syringe with stirring. Stirring was continued for 24 h at room temperature. The reaction mixture was filtered and the precipitate was rinsed with dichloromethane. Organic layers were treated successively with aqueous saturated sodium bicarbonate solution, water and dried over sodium sulphate. Solvents were removed by evaporation under reduced pressure and the crude product was purified by chromatography on silica gel using acetone/dichloromethane (90/10)

to give 0.44 g of (VIa) as white needles. Yield. 52%. mp. 60°C. Anal. found: C, 57.6; H, 7.18. $C_{13}H_{19}O_2SiP$ (266.36). Calc.: C, 57.7; H, 7.19%.

^{31}P RMN δ: 60.73 (s)
IR (CCl_4): 3060, 2959, 2362, 1438 (P—C_6H_5), 1395, 1253, 1230 ($SiMe_3$), 1187, 1154, 1111, 912 cm^{-1}. ^1H NMR (400 MHz) δ: 0.11 (s, 9H, $SiMe_3$). 2.43 (m, 4H, H^2, $H^{2'}$, H^4, $H^{4'}$), 3.56 (dd, 1H, H^5), 7.64 (m, 6H, C_6H_5). ^{13}C NMR δ: −3.77 (s, $SiMe_3$), 32.84 (C^2, d, J = 66.56 Hz), 33.44 (C^4, d, J = 61.01 Hz), 57.75 (C^5, d, J = 6.1 Hz), 128.44 (C^9, d, J = 12.28 Hz), 131.09 (C^8, d, J = 10.72 Hz), 131.68 (C^{10}, d, J = 2.65 Hz), 133.1 (C^7, d, J = 93.8 Hz). GSMS m/e (relative intensity): 266 (40) $(M)^+$, 251 (32) $(M—Me)^+$, 237 (68) $(M—29)^+$, 141 (9) $[PhP(O)OH]^+$, 124 (7) $(Ph—P)^+$, 77 (45) $(C_6H_5)^+$, 75 (38) $(Me_2SiOH)^+$, 73 (100) $(Me_3Si)^+$, 43 (32) $(MeSi)^+$.
Dipole moment: 7.04 D.

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