Heteroatom Chemistry
Volume 10, Number 3, 1999

Reactivity of Substituted 3-(Diethylphosphonyl)-1-(trialkylsilyl)alka-1,3-dienes: Regioselective Epoxidation and Cyclopropanation Reactions

Fabien Chevalier, Hashim Al-Badri, and Noël Collignon

Laboratoire des Composés Organophosphorés de l'INSA, Groupe d'Hétérochimie Organique de l'IRCOF, UPRES A 6014 CNRS, Place E. Blondel, BP 08, 76131 Mont-Saint-Aignan Cedex, France

Received 2 July 1998; revised 2 October 1998

ABSTRACT: *When treated with electrophilic m-CPBA reagent, dienes* **1** *were efficiently epoxidized at the silylated 1,2-double bond exclusively. Otherwise, regioselective cyclopropanation of the phosphonylated 3,4-double bond was achieved by using the nucleophilic Corey's reagent.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10:231–236, 1999

INTRODUCTION

Recently, we described an efficient and stereoselective synthesis of variously substituted dienes **1** [1]. An interesting feature of these dienes is the difference in electron density between the two double bonds, which should allow a regioselective functionalization of the conjugated system. Owing to the opposite orienting effects of the two heteroatomic groups, it can be expected that the electron-rich silylated 1,2-double bond should be more subject to electrophilic attack, whereas the electron-deficient phosphonylated 3,4-double bond should be more subject to nucleophilic attack (Scheme 1).

To study the ability of conjugated phosphonodienes **1** to undergo regioselective functionalization, we selected two typical reactions, namely, epoxidation and cyclopropanation reactions, which involve nucleophilic as well as electrophilic reagents. For example, addition reactions of peroxide anions [2] or of sulfur ylides [3] to electron-deficient double bonds are widely used for building epoxide or cyclopropane rings, respectively. On the other hand, the same target can be attained from electron-rich double bonds, by using peracids [4] or carbenes [5]. In this work, we successively studied the epoxidation and the cyclopropanation reactions of compounds **1,** using *m*-chloroperbenzoic acid (*m*-CPBA) and dimethylsulfoxonium methylide (DMSY), as three-membered ring-forming reagents.

RESULTS AND DISCUSSION

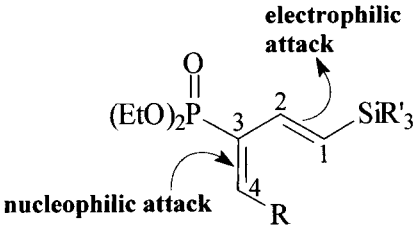
Regioselective m-CPBA-epoxidation of Phosphonodienes **1**

When treated at 0°C, for about 24 hours, with *m*-CPBA in dichloromethane, phosphonodienes **1** were efficiently oxidized into the corresponding epoxyalkenylphosphonates **2** (Scheme 2), as proved by ^{1}H, ^{13}C, and ^{31}P NMR spectra (Tables 1, 3, and 4 and Experimental section). ^{31}P NMR spectra showed chemical shift values between $\delta = 15$ and 17, which are characteristic of an alkenylphosphonate environment [6]. Moreover, $^{3}J_{H_1H_2}$ coupling constant values of the order of 3 to 4 Hz, determined on the ^{1}H NMR spectra of **2,** are in agreement with a *trans*-configuration of the epoxide ring [7], resulting from the stereoselective *syn*-addition of the peracid to the *E*-1,2-

Correspondence to: Noël Collignon
 CCC 1042-7163/99/030231-06

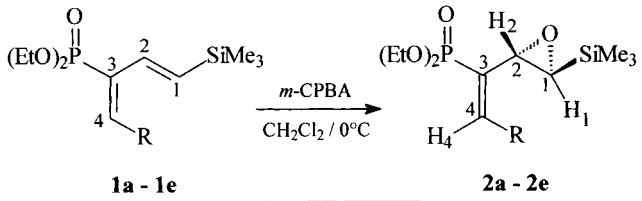
double bond of **1** [8]. These results confirm the selective reactivity of the 1,2-double bond of phosphonodienes **1,** in the presence of the electrophilic epoxidation reagent [9] and open an interesting route to new epoxysilylalkenylphosphonates **2** of promising synthetic utility [10].

As expected, the configuration of the 3,4-double bond of the starting diene **1** was strictly preserved in the epoxyalkene **2.** The (*E*)-configuration of the 3,4-double bond in the purified product **2** was unambiguously assigned by measuring the $^3J_{H_4P}$ coupling constant in ^{1}H NMR spectra [11,12]. The observed values (22.6–24.0 Hz, Table 1) were very close to the ones of the parent diene [1].



1

SCHEME 1



1a - 1e **2a - 2e**

1, 2	R
a	Ph
b	4-Cl-C_6H_4
c	4-Me-C_6H_4
d	4-F_3C-C_6H_4
e	Me

SCHEME 2

TABLE 1 Synthesis of 3-(Diethylphosphonyl)-1,2-epoxy-1-(trimethylsilyl)alk-3-enes **2**

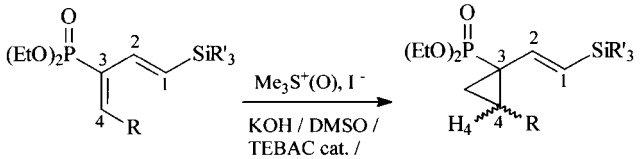
Run	Product	^{31}P NMR ($CDCl_3$) δ (ppm)	^1H NMR ($CDCl_3$) $^3J_{H_1H_2}$	^1H NMR ($CDCl_3$) $^3J_{H_4P}$ (Hz)	Yield (%) in Purified Product[a]
1	**2a**	15.7	4.1	24.0	76
2	**2b**	15.4	3.8	23.8	75
3	**2c**	16.1	3.8	23.4	72
4	**2d**	14.6	3.6	—[b]	67
5	**2e**	15.9	3.9	22.6	81

[a]Product purified by column chromatography over SiO_2 (eluent:ether). Purity controlled by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry.
[b]Value not determined; overlapping of H_4 and aromatic proton signals.

Regioselective DMSY-Cyclopropanation of Phosphonodienes **1**

In a second set of experiments, we decided to examine the reactivity of phosphonodienes **1** toward dimethylsulfoxonium methylide, the nucleophilic Corey's reagent [13,14]. To the best of our knowledge, apart from the work of Minami *et al.* [15] dealing with the cyclopropanation of 4-phenyl-buta-1,3-dienylphosphonates bearing electronegative substituents on the carbon-1, no other examples of reaction of DMSY with butadienylphosphonates have been reported [16].

The cyclopropanation procedure with DMSY typically involves the use of an alkali metal hydride in dry THF, as basic medium [14]. However, a recent alternative, using a mixture of KOH and DMSO in the presence of a phase-transfer catalyst (PTC) as a "super-basic" medium, proved to be effective for the stereoselective cyclopropanation of some α,β-unsaturated ketones [17]. We chose to apply this last procedure to dienes **1,** which were treated, at room temperature, with stoichiometric amounts of KOH and of trimethylsulfoxonium iodide and with a catalytic amount of triethylbenzylammonium chloride (TEBAC), in DMSO as solvent. The reaction was monitored by ^{31}P MMR spectroscopy and was complete after about 20 hours. Usual workup led to crude cyclopropylphosphonates **3** (Scheme 3), which were purified by column chromatography and whose



1a - 1d, 1f **3a - 3d, 3f**

1, 3	R	R'
a	Ph	Me
b	4-Cl-C_6H_4	Me
c	4-Me-C_6H_4	Me
d	4-F_3C-C_6H_4	Me
f	Me	*i*-Pr

SCHEME 3

structures were determined by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy (Tables 2–4 and Experimental section). However, when diene **1e** was treated under the same conditions, the ^{31}P NMR spectrum of the crude mixture exhibited several peaks near $\delta = 26$ to 28, suggesting a desilylation process; after usual workup, we were not able to isolate the expected cyclopropyl derivative. We found that replacing the trimethylsilyl group by the bulky tri-*iso*-propylsilyl one, in the starting diene (**1f**, see Experimental part), allowed the cyclopropanation reaction to proceed smoothly, giving the expected phosphonate **3f** in good yield, without any desilylation reaction (Table 2, run 5).

NMR spectra of compounds **3** unambiguously proved the presence of the 3,4-methylene bridge, as well as an alkenylsilane of (*E*) configuration. These results imply a strict 3,4- regioselective attack of the cyclopropanation reagent on the diene **1** and confirm the lack of reactivity of the alkenylsilane moiety, under the experimental conditions.

Moreover, spectra and chromatograms showed that compounds **3,** prepared from dienes **1** of (3*E*) configuration, consist of mixtures of *trans*- and *cis*-cyclopropane stereoisomers, which were formed with moderate diastereoselectivity (52–68%, Table 2, runs 1 to 4), or without any selectivity in the case of **3f** [18]. The relative configuration of the diastereomers was deduced from ^{1}H and ^{13}C NMR spectra, by measuring the $^{3}J_{H_4P}$ and $^{3}J_{CiP}$ coupling constants (Table 2 and Scheme 4), which were assumed to follow a Karplus-type relationship [19–21]. On the one hand, $^{3}J_{H_4P}$ values varing from 15 to 16.5 Hz for the *trans*-**3** isomer and from 11 to 12 Hz for the *cis*-**3** isomer (corresponding to a *cis*- and a *trans*-arrangement of the P-C_3-C_4-H_4 bonds, respectively) are in agreement with previously reported results [22,23]. On the other hand, in the ^{13}C NMR spectra, the $^{3}J_{CiP}$ values noted for the *trans*-**3** isomer (from 1.9 to 2.8 Hz) and for the *cis*-**3** isomer (from 5.0 to 5.9 Hz) fulfill the $^{3}J_{CiP\text{-}cis} > {}^{3}J_{CiP\text{-}trans}$ relation, in agreement with a Karplus-type relationship applied to substituted cyclopropylphosphonates [24]. Moreover, as expected, nonequivalence between H_x and H_Y protons is observed in ^{1}H NMR spectra of **3.**

TABLE 2 Synthesis of 3-(Diethylphosphonyl)-3,4-methylene-1-(trialkylsilyl)alk-1-enes **3**

Run	Product	^{31}P NMR ($CDCl_3$) δ (ppm) trans/cis (ratio)[a]	^{1}H NMR ($CDCl_3$) $^{3}J_{H_4P}$ (Hz) trans	^{1}H NMR ($CDCl_3$) $^{3}J_{H_4P}$ (Hz) cis	^{13}C NMR ($CDCl_3$) $^{3}J_{CiP}$ (Hz) trans	^{13}C NMR ($CDCl_3$) $^{3}J_{CiP}$ (Hz) cis	Yield (%) in Purified Product[b]
1	**3a**	25.1/23.0 (84/16)	16.5	11.8	2.7	5.9	77
2	**3b**	25.1/23.4 (78/22)	15.6	11.0	2.8	5.9	58
3	**3c**	25.7/23.7 (76/24)	16.3	11.4	2.7	5.8	96
4	**3d**	24.8/22.9 (76/24)	16.2	11.2	1.9	5.6	68
5	**3f**	27.3/26.8 (48/52)	—[c]	—[c]	1.9	5.0	87

[a]Determined in the crude mixture.
[b]Product (as *trans*/*cis* mixture) purified by flash chromatography over SiO_2 (eluent:ether). In most cases, this purification process did not significantly alter the crude *trans*/*cis* ratio. Purity controlled by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry.
[c]Values not determined; overlapping of H_4 and *i*-propyl signals.

CONCLUSION

In summary, this work proves the remarkable difference in the reactivity of the two double bonds of alka-1,3-dienes **1,** substituted at the 1- and 3-positions, respectively, by trialkylsilyl and diethylphosphonyl groups, toward electrophilic and nucleophilic reagents, allowing regioselective functionalization of the conjugated system. These possibilities have been illustrated by the regioselective electrophilic epoxydation of the silylated 1,2-double bond and by the regioselective nucleophilic cyclopropanation of the phosphonylated 3,4-double bond of dienes **1,** each of these reactions leading to new useful epoxy- or cycloalkylalkenylphosphonates, respectively.

EXPERIMENTAL

General

All reactions were carried out using standard techniques. Solvents were purified by conventional methods prior to use. Reagents were purchased from common commercial suppliers. TLC was performed on Merck 60 F-254 silica-gel plates and column chromatography over silica gel (230–400 mesh). Mass spectra were recorded on a Jeol AX 500 spectrometer, under electronic impact at 70 eV (*m*/*z*, and relative abundance in %, are given) or under chemical ionization at 200 eV for HRMS measurements. NMR spectra were recorded on a Bruker AC 200 spectrometer operating at 200 MHz for proton, 50.3 MHz for carbon, and 81.01 MHz for phosphorus; chemical shifts (δ) are expressed in ppm relative to TMS for ^{1}H and ^{13}C nuclei and to H_3PO_4 for ^{31}P nucleus; coupling constants (*J*) are given in Hertz; coupling multiplicities are reported using conventional abbreviations.

TABLE 3 Selected ^{1}H NMR ($CDCl_3$) Data for **2** and **3**:δ, Multiplicity (J)[a]

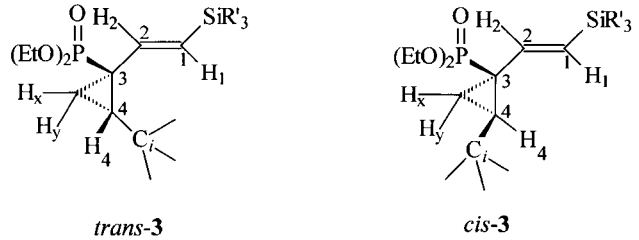
Product	H_1	H_2	H_4
2a	2.2, d (4.1)	3.5, dd (16; 4.1)	7.5, d (24)
2b	2.5, d (3.8)	3.5, dd (15; 3.8)	7.5, d (23.8)
2c	2.6, d (3.8)	3.6, dd (15.7; 3.8)	7.6, d (23.4)
2d	2.5, d (3.6)	3.5, dd (14.5; 3.6)	—[b]
2e	2.2, d (3.9)	3.3, dd (10.7; 3.9)	6.7, dq (22.6; 7.2)
trans-**3a**	5.7, dd (18.8; 2.2)	5.5, dd (18.8; 7.9)	2.8, ddd (16.5; 8.9; 6.7)
cis-**3a**	5.8, dd (18.2; 2.2)	6.4, dd (18.2; 7.8)	2.4, ddd (11.8; 8.8; 7.3)
trans-**3b**	5.7, d (18.7)	5.5, dd (18.7; 6.9)	2.8, ddd (15.6; 8.7; 6.2)
cis-**3b**	5.8, dd (18.3; 2.5)	6.4, dd (18.3; 7.5)	2.4, ddd (11; 9.4; 7.3)
trans-**3c**	5.7, dd (18.9; 2.2)	5.5, dd (18.9; 7.8)	2.8, ddd (16.3; 9; 6.1)
cis-**3c**	5.8, dd (18.3; 2.3)	6.4, dd (18.3; 7.4)	2.4, ddd (11.4; 8.8; 7.2)
trans-**3d**	5.7, dd (18.6; 2.6)	5.6, dd (18.6; 6.6)	2.9, ddd (16.2; 8.4; 6.5)
cis-**3d**	5.8, dd (18.5; 2.3)	6.4, dd (18.5; 7.4)	2.4, ddd (11.2; 9; 7.3)
trans-**3f**	5.7, dd (19; 2.8)	6.3, dd (19; 6.2)	—[c]
cis-**3f**	5.5, dd (18.5; 2.5)	6.3, dd (18.5; 7)	—[c]

[a]Other parts of the spectra are in accordance with the molecular structures.
[b]Values not determined; overlaping of H_4 and aromatic proton signals.
[c]Values not determined; overlaping of H_4 and *i*-propyl proton signal.

TABLE 4 Selected $^{13}C\{^1H\}$ NMR ($CDCl_3$) Data for **2** and **3**: δ, Multiplicity (J)[a]

Product	C_1	C_2	C_3	C_4
2a	52.5, d (7.4)	52.8, d (22)	128.1, d (180.4)	146.6, d (9.1)
2b	52.3, d (8.3)	53.1, d (2)	128.9, d (180.4)	145.0, d (9.5)
2c	52.7, d (7.5)	53.0, d (2.2)	127.0, d (180.9)	146.7, d (9.3)
2d	52.3, d (8.3)	53.3, d (2)	131.1, d (179.4)	142.3, d (9.3)
2e	51.6, d (13.8)	51.7, d (2)	127.8, d (182.6)	146.1, d (8.9)
trans-**3a**	135.5, d (7.7)	138.0, d (2.3)	27.6, d (185.8)	28.3, d (2.7)
cis-**3a**	129.3, d (7.9)	143.5, d (3.7)	28.9, d (190.1)	32.6, d (3)
trans-**3b**	136.1, d (7.7)	137.5, d (2.2)	27.8, d (186.1)	27.6, d (2.8)
cis-**3b**	129.8, d (7.9)	142.9, d (3.2)	28.9, d (190.2)	31.7, d (3)
trans-**3c**	135.3, d (7.7)	138.1, d (2.3)	27.5, d (185.4)	28.0, d (2.7)
cis-**3c**	128.9, d (7.9)	143.6, d (3.7)	28.9, d (190.1)	32.3, d (3.2)
trans-**3d**	136.4, d (7.8)	139.0, ~s	28.3, d (186.1)	27.9, d (2.7)
cis-**3d**	130.1, d (7.8)	142.8, d (3.3)	29.2, d (189.6)	31.8, d (3.1)
trans-**3f**	129.7, d (8.5)	140.8, d (1.3)	25.2, d (185.5)	17.8, d (2.7)
cis-**3f**	122.0, d (7.9)	146.3, d (2.9)	25.4, d (186.9)	23.3, d (2)

[a]Other parts of the spectra are in accordance with the molecular structures.



trans-**3** *cis*-**3**

SCHEME 4

Preparation of the (1E, 3E)-3-(Diethylphosphonyl)-1-(triisopropylsilyl)penta-1,3-diene **1f**

This compound was prepared according to Ref. [1], using triisopropylsilyl chloride in place of trimethylsilyl chloride, and was obtained, as an oil, in 57% yield, after purification by column chromatography over SiO_2 (eluent:ether). **1f**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): 17.3; ^{1}H NMR ($CDCl_3$): 0.8–1.3 (m, 27H, $[(C\underline{H}_3)_2C\underline{H}]_3Si$ and $(C\underline{H}_3CH_2O)_2P$), 1.9 (dd, J_{H_5P} = 3.1, $J_{H_5H_4}$ = 7.3, 3H, $C\underline{H}_3$-C_4), 3.8–4.0 [m, 4H,

$(CH_3C\underline{H}_2O)_2P$], 6.1 (d, $J_{H_1H_2}$ = 19.5, 1H, $\underline{H}_1$), 6.6 (dd, J_{H_2P} = 25.5, $J_{H_2H_1}$ = 19.5, 1H, $\underline{H}_2$), 6.7 (dd, J_{H_4P} = 21.0, $J_{H_4H_5}$ = 7.3, 1H, $\underline{H}_4$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 10.6 [s, $[(CH_3)_2\underline{C}H]_3Si$), 14.6 (d, J = 18.5, $\underline{C}_5$), 16.0 and 16.1 [2d, J = 7.0, J = 6.6, $(\underline{C}H_3CH_2O)_2P$], 18.4 (s, $[(\underline{C}H_3)_2CH]_3Si$), 61.1 and 61.3 [2d, J = 5.4, J = 5.2, $(CH_3\underline{C}H_2O)_2P$], 129.9 (d, J = 171.8, $\underline{C}_3$), 130.9 (d, J = 5.1, $\underline{C}_2$), 136.4 (d, J = 10.9, $\underline{C}_1$), 143.8 (d, J = 10.2, $\underline{C}_4$); MS: 360 (2), 317 (50), 289 (14), 261 (100), 217 (22), 177 (11), 151 (8), 123 (19), 109 (8), 67 (18), 59 (15), 40 (5); HRMS calcd for $C_{18}H_{37}O_3PSi$: 360.2249; found: 360.2245.

Preparation of (1-trans)-(3E)-3-(Diethylphosphonyl)-1,2-epoxy-1-(trimethylsilyl)alk-3-enes **2**

Typical Procedure for **2d.** To a stirred solution of phosphonodiene **1d** (0.6 g, 1.48 mmol) in dichloromethane (6 mL) cooled at 0°C was added *m*-CPBA (0.44 g, 1.78 mmol) in portions, and the reaction mixture was allowed to stir for 24 hours (the reaction was monitored by ^{31}P NMR). The resulting mixture was washed with aqueous solutions of Na_2SO_3 (3×5 mL), Na_2CO_3 (3×5 mL), and brine (3×5 mL), successively. The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel (eluent:ether) giving the pure product as an oil (0.42 g, 67% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 14.6; ^1H NMR ($CDCl_3$): 0.0 [s, 9H, $(C\underline{H}_3)_3Si$], 1.1–1.3 [m, 6H, $(C\underline{H}_3CH_2O)_2P$], 2.5 (d, $J_{H_1H_2}$ = 3.6, 1H, $\underline{H}_1$), 3.5 (dd, J_{H_2P} = 14.5, $J_{H_2H_1}$ = 3.6, 1H, $\underline{H}_2$), 4.0–4.2 [m, 4H, $(CH_3CH_2O)_2P$], 7.4–7.6 (m, 4H, $C_6\underline{H}_4$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): −4.0 (s, $(\underline{C}H_3)_3Si$), 16.0 and 16.1 [2d, J = 6.1, J = 6.4, $(\underline{C}H_3CH_2O)_2P$], 52.3 (d, J = 8.3, $\underline{C}_1$), 53.3 (d, J = 2.0, $\underline{C}_2$), 62.0 and 62.1 [2d, J = 6.0, J = 5.4, $(CH_3\underline{C}H_2O)_2P$], 123.6 (q, J = 272.1, $\underline{C}F_3$), 124.9 (q, J = 4.0, m-$\underline{C}_{arom}$), 131.1 (d, J = 179.4, $\underline{C}3$), 129.6 (q, J = 1.0, o-$\underline{C}_{arom}$), 130.5 (q, J = 32.7, p-$\underline{C}_{arom}$), 137.9 (dq, J_{CP} = 22.0, J_{CF} = 1.0, i-$\underline{C}_{arom}$), 142.3 (d, J = 9.3, $\underline{C}_4$); MS: 422 (28), 393 (64), 365 (26), 333 (30), 321 (27), 277 (25), 265 (15), 235 (16), 193 (46), 183 (89), 155 (30), 121 (36), 81 (17), 73 (100), 45 (34); HRMS: calcd for $C_{18}H_{26}F_3O_4PSi$: 422.1290; found: 422.1269.

Preparation of (1E)-3-(Diethylphosphonyl)-3,4-methylene-1-(trialkylsilyl)alk-1-enes **3**

Typical Procedure for **3a.** DMSO (6 mL) was added, under argon, to a mixture of phosphonodiene **1a** (0.5 g, 1.48 mmol), KOH in pellets (0.08 g, 1.48 mmol), TEBAC (0.01 g), and trimethylsulfoxonium iodide (0.33 g, 1.48 mmol). The mixture was vigorously stirred for about 20 hours (the reaction was monitored by ^{31}P NMR). The resulting mixture was then poured into water and extracted with ether (3×5 mL). The crude mixture was purified by flash chromatography over silica gel (eluent:ether), giving the oily pure product (0.4 g, 77% yield), as a mixture of *trans*- and *cis*-isomers, in a ratio of 84/16, respectively.

trans-**3a.** $^{31}P\{^1H\}$ NMR ($CDCl_3$): 25.1; ^1H NMR ($CDCl_3$): −0.2 [s, 9H, $(C\underline{H}_3)_3Si$], 1.1–1.3 [m, 6H, $(C\underline{H}_3CH_2O)_2P$], 1.5 (ddd, $J_{H_xH_y}$ = 4.9, $J_{H_xH_4}$ = 6.7, J_{H_xP} = 12.1, 1H, $\underline{H}_x$), 1.7 (ddd, $J_{H_yH_x}$ = 4.9, $J_{H_yH_4}$ = 8.9, J_{H_yP} = 16.1, 1H, $\underline{H}_y$), 2.8 (ddd, $J_{H_4H_x}$ = 6.7, $J_{H_4H_y}$ = 8.9, J_{H_4P} = 16.5, 1H, $\underline{H}_4$), 4.0–4.2 [m, 4H, $(CH_3C\underline{H}_2O)_2P$], 5.5 (dd, J_{H_2P} = 7.9, $J_{H_2H_1}$ = 18.8, 1H, $\underline{H}_2$), 5.7 (dd, J_{H_1P} = 2.2, $J_{H_1H_2}$ = 18.8, 1H, $\underline{H}_1$), 6.8–7.2 (m, 5H, $C_6\underline{H}_5$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): −1.8 [s, $(\underline{C}H_3)_3Si$], 14.0 (d, J = 2.3, $\underline{C}H_xH_y$), 16.1 and 16.2 [2d, J = 7.7, J = 7.5, $(\underline{C}H_3CH_2O)_2P$], 27.6 (d, J = 185.8, $\underline{C}_3$), 28.3 (d, J = 2.7, $\underline{C}_4$), 62.0 [d, J = 6.0, $(CH_3\underline{C}H_2O)_2P$], 126.2 (s, p-$\underline{C}_{arom}$), 127.5 (s, m-$\underline{C}_{arom}$), 128.9 (s, o-$\underline{C}_{arom}$), 135.3 (d, J = 2.7, i-$\underline{C}_{arom}$), 135.5 (d, J = 7.7, $\underline{C}_1$), 138.0 (d, J = 2.3, $\underline{C}_2$); MS: 352 (35), 323 (8), 275 (15), 261 (39), 203 (27), 171 (15), 141 (100), 121 (33), 115 (25), 73 (65), 59 (13), 45 (21); HRMS: calcd for $C_{18}H_{29}O_3PSi$: 352.1624; found: 352.1625.

cis-**3a.** $^{31}P\{^1H\}$ NMR ($CDCl_3$): 23.0; ^1H NMR ($CDCl_3$): 0.1 [s, 9H, $(C\underline{H}_3)_3Si$], 1.0–1.2 [m, 6H, $(C\underline{H}_3CH_2O)_2P$], 1.5 (ddd, $J_{H_xH_y}$ = 4.7, $J_{H_xH_4}$ = 8.8, J_{H_xP} = 8.8, 1H, $\underline{H}_x$), 2.0 (ddd, $J_{H_yH_x}$ = 4.7, $J_{H_yH_4}$ = 7.3, J_{H_yP} = 16.2, 1H, $\underline{H}_y$), 2.4 (ddd, $J_{H_4H_x}$ = 8.8, $J_{H_4H_y}$ = 7.3, J_{H_4P} = 11.8, 1H, $\underline{H}_4$), 3.6–4.0 [m, 4H, $(CH_3C\underline{H}_2O)_2P$], 5.8 (dd, $J_{H_1H_2}$ = 18.2, J_{H_1P} = 2.2, 1H, $\underline{H}_1$), 6.4 (dd, J_{H_2P} = 7.8, $J_{H_2H_1}$ = 18.2, 1H, $\underline{H}_2$), 7.2–7.4 (m, 5H, $C_6\underline{H}_5$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): −1.4 [s, $(\underline{C}H_3)_3Si$], 16.0 [d, J = 6.2, $(\underline{C}H_3CH_2O)_2P$], 16.5 (d, J = 1.8, $\underline{C}H_xH_y$), 28.9 (d, J = 190.1, $\underline{C}_3$), 32.6 (d, J = 3.0, $\underline{C}_4$), 61.1 and 61.5 [2d, J = 6.0, J = 6.6, $(CH_3\underline{C}H_2O)_2P$], 126.5 (s, p-$\underline{C}_{arom}$), 127.5 (s, m-$\underline{C}_{arom}$), 129.3 (d, J = 7.9, $\underline{C}_1$), 129.6 (s, o-$\underline{C}_{arom}$), 136.3 (d, J = 5.9, i-$\underline{C}_{arom}$), 143.5 (d, J = 3.7, $\underline{C}_2$).

REFERENCES

[1] Chevalier, F.; Al-Badri, H.; Collignon, N. Bull Soc Chim Fr 1997, 134, 801.

[2] March, J. Advanced Organic Chemistry; Wiley: New York, 1992; p 827 4th ed., and references cited therein.

[3] Metzner, P.; Thuillier, A. Sulfur Reagents in Organic Synthesis; Academic: London, 1994; p 143 and references cited therein.

[4] Hudlicky, M. Oxidations in Organic Chemistry;

American Chemical Society: Washington, 1990; p 60 and references cited therein.
[5] March, J. Advanced Organic Chemistry; Wiley: New York, 1992; 4th ed. p. 866 and references cited therein.
[6] Tebby, J. C. In Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; p 34.
[7] Value of 3.2 Hz was reported for $^3J_{HH}$ in *trans*-*β*-trimethylsilylstyrene oxide. Eisch, J. J.; Galle, J. E. J Org Chem 1976, 41, 2618 (only one enantiomer of **2** is represented in Scheme 2).
[8] In a recent reinvestigation of the epoxidation mechanism of alkenes by peracids, the proposed oxygen transfer *via* a nonpolar concerted transition state confirms the standard Bartlett's mechanism. Angelis, Y. S.; Orfanopoulos, M. J Org Chem 1997, 62, 6083 and references cited therein.
[9] Preliminary experiments showed the total lack of reactivity of the 3,4-double bond as well as of the 1,2-double bond of **1** toward the usual nucleophilic epoxidation reagent: alkaline hydrogen peroxide.
[10] For useful synthetic applications of *α*,*β*-epoxysilyl groups, see, for example, Colvin, E. W. Silicon in Organic Synthesis; R. E. Krieger Publ. Comp.: Malabar, 1985; p 83 and references cited therein.
[11] Kenyon, G. L.; Westheimer, F. H. J Am Chem Soc 1966, 88, 3557.
[12] Benezra, C.; Nseic, S.; Ourisson, G. Bull Soc Chim Fr 1967, 1140.
[13] Corey, E. J.; Chaykovsky, M. J Am Chem Soc 1965, 87, 1353.
[14] Gololobov, Y. G.; Nesmeyanov, A. N.; Lysenko, V. P.; Boldeskul, I. E. Tetrahedron 1987, 43, 2609 and references cited therein.
[15] Minami, T.; Yamanouchi, T.; Tokumasu, S.; Hirao, I. Bull Chem Soc Jpn 1984, 57, 2127.
[16] Regioselective cyclopropanation of other electron-deficient conjugated dienes have recently attracted considerable interest in organic synthesis; see, for example, Löfström, C. M. G.; Ericsson, A. M.; Bourrinet, L.; Juntunen, S. K.; Bäckvall, J. E. J Org Chem 1995, 60, 3586 and references cited therein.
[17] Shostakovsky, V. M.; Carlson, R. M. Synth Commun 1996, 26, 1785.
[18] (a) The degree of diastereoselectivity of the cyclopropanation reaction of electron-deficient unsaturated substrates, using DMSY as reagent, seems to be very dependent on the nature of the substituents of the double bond; see, for example, (b) Kaiser, C.; Trost, B. M.; Beeson, J.; Weinstock, J. J Org Chem 1965, 30, 3972; (c) Nozaki, H.; Itô, H.; Tunemoto, D.; Kondô, K. Tetrahedron 1966, 22, 441; (d) Landor, S. R.; Punja, N. J Chem Soc 1967, 2495; (e) Merz, A.; Märkl, G. Angew Chem Int Ed 1973, 12, 845.
[19] Bentrude, W. G.; Setzer, W. N. In Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis; Verkade, J. G., Quin, L. D., Ed.; VCH: Deerfield Beach, FL, 1987; p 365.
[20] Benezra, C. J Am Chem Soc 1973, 95, 6890.
[21] Thiem, J.; Meyer, B. Org Magn Res 1978, 11, 50.
[22] Samitov, Y. Y.; Gareev, R. D.; Stabrovskaya, I. A.; Pudovik, A. N. Zh Obshch Khim 1972, 42, 1227.
[23] Maas G. Phosphorus and Sulfur 1983, 14, 143.
[24] To the best of our knowledge, few examples of $^3J_{CP}$ vicinal coupling constants that belong to cyclopropyl phosphonates have been reported. In Ref. [15], values of $^3J_{CP}$ varying from 3.4 to 4.3 Hz (about 2 Hz lower than values observed for *cis*-**3** isomers) are given for *cis*-cyclopropyl phosphonates bearing electron-withdrawing *α*-substituents. Significant decrease of the magnitude of $^3J_{CP}$ by electronegative *α*-substituents was in fact previously observed (see Ref. [21]).