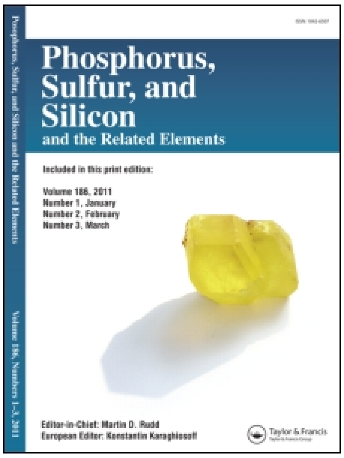

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STEREOSELECTIVE SYNTHESIS OF DIMETHYL-AND DIETHYL-E-2-(TRIMETHYLSILYL)VINYL PHOSPHONATES AND THEIR USE IN THE DIELS-ALDER REACTION

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Communication

STEREOSELECTIVE SYNTHESIS OF DIMETHYL- AND DIETHYL-E-2-(TRIMETHYLSILYL)VINYL PHOSPHONATES AND THEIR USE IN THE DIELS-ALDER REACTION

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Dimethyl E-2-(trimethylsilyl)vinyl phosphonate **1** and diethyl E-2-(trimethylsilyl)vinyl phosphonate **2** are obtained stereoselectively by Pd (0) coupling of an E/Z mixture of (2-trimethylsilyl)vinyl bromide **3** and dimethyl phosphite or diethyl phosphite, respectively. Their use in the Diels-Alder reaction with cyclopentadiene is described, and coordination of aluminum trichloride to the phosphonyl group favors the endo stereoselectivity.

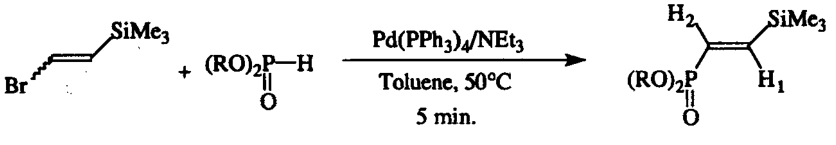
Key words: Vinyl phosphonates; vinyl silanes; palladium-catalyzed carbon-phosphorus bond formation; Diels-Alder reaction; organophosphorus dienophiles; Lewis acids.

Functionalized vinyl phosphonates have been used with success in organic synthesis, mainly as Horner-Wadsworth-Emmons reagents[1,2] and dienophiles in the Diels-Alder reaction.[3] Among the different synthetic methods reported,[2] the coupling of different vinylic bromides with a dialkyl phosphite in the presence of a catalytic amount of palladium tetrakis(triphenyl phosphine) is of interest. This reaction has been shown to proceed with complete retention of configuration at the double bond,[4] thus allowing a stereoselective entry to α,β-unsaturated phosphorus compounds; furthermore, the use of a chiral dialkyl phosphite leads to the corresponding chiral vinyl phosphonate with complete retention of configuration at the phosphorus atom.[5] This methodology has been widely used for the synthesis of vinylic phosphonates as well as some (carboalkoxy-vinyl) phosphonates[6]; more recently, diethyl (1-trimethylsilyl)vinyl phosphonate[7a] and (1-trimethylsilyl) 2-alkylvinyl phosphonates[7b] have been reported. We wish to describe here the synthesis of dimethyl 2-(trimethylsilyl)vinyl phosphonate **1** and diethyl 2-(trimethylsilyl)vinyl phosphonate **2** from 2-(trimethylsilyl)vinyl bromide **3** (Equation 1), and their use in a Diels-Alder reaction with cyclopentadiene.

1 and **2** were obtained only as the trans isomers (as shown by examination of $^3J_{HH}$ coupling constants) although **3** always exists as a Z/E mixture (10:90). This fact may indicate that the coupling reaction is very sensitive to the steric hindrance in the substrate: E-3 is less hindered so that the palladation step can proceed faster. This was already suggested by the different reactivities for E and Z isomers of vinylic bromides, as reported previously.[4] The trans structures for **1** and **2** were deduced from the coupling constants of protons H_1 and H_2 (refer to Equation 1 for proton numbering) with the phosphorus atom, and by comparison with the reported data for related compounds.[8]

In order to illustrate one of the possible uses of these compounds, we investigated the Diels-Alder reaction of **1** and **2** with cyclopentadiene (Scheme I).

The reactions were carried out in refluxing toluene as well as in dichloromethane at room temperature in the presence of one equivalent of anhydrous aluminum trichloride, since Lewis acids have been shown to be good activators for vinyl

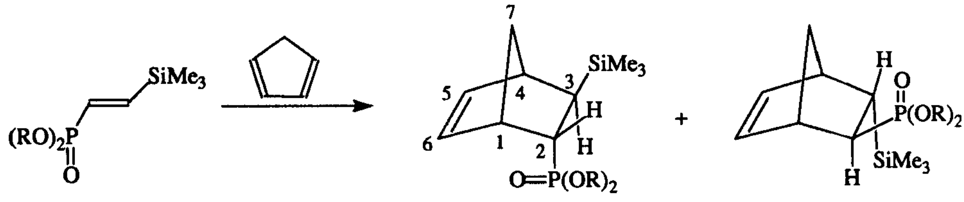


3

1 (R=CH3) 80% yield

2 (R=C2H5) 76% yield

Equation 1



		4a (endo)		4b (exo)
1 (R=CH3)	Toluene, reflux (24 hrs, 66% yield)	35	:	65
	$AlCl_3$ (1 equiv.)/CH_2Cl_2/r.t. (24 hrs, 79% yield)	85	:	15
		5a (endo)		5b (exo)
2 (R=C2H5)	Toluene, reflux (24 hrs, 72% yield)	40	:	60
	$AlCl_3$ (1 equiv.)/CH_2Cl_2/r.t. (24 hrs, 81% yield)	88	:	12

Scheme I

phosphonates in Diels-Alder reactions.[9] The cycloadditions gave rise to the endo (**4a, 5a**) and exo (**4b, 5b**) adducts whose structures have been assigned by comparison with reported NMR data.[9,10] Interestingly, the thermal cycloadditions gave a 35:65 mixture of **4a/4b**, and a 40:60 mixture of **5a/5b** respectively, whereas the Lewis acid promoted reaction led to a reversed stereoselectivity (**4a/4b** = 85:15, **5a/5b** = 88:12). Here again, the use of $AlCl_3$ increases the endo/exo ratio, with concomitant rate increase, as reported previously.[9] However, the steric hindrance from the trimethylsilyl group decreases the reactivity (vs. dimethyl or diethyl vinylphosphonate), while the dienophilic character is not enhanced, according to the low reactivity of trimethylsilyl vinyl silane in Diels-Alder reactions.[11]

The replacement of the β proton by the bulkier TMS group in the catalyzed Diels-Alder reactions does not affect the endo/exo ratios. For comparison, thermal and $AlCl_3$-promoted cycloaddition of diethyl vinyl phosphonate gave endo/exo ratios of 45:55 and 85:15, respectively,[9] while cycloadditions of dimethyl vinyl phosphonate gave endo/exo ratios of 50:50 (thermal reaction) and 87:13 ($AlCl_3$-catalyzed reaction.[12] This result is rather surprising due to the steric repulsion between the TMS group and the methylene moiety of cyclopentadiene in the endo transition state. However, these facts can be explained by assuming that the stereoselectivity of the $AlCl_3$-promoted reactions is controlled by the phosphonyl group, coordinated to the Lewis acid.

In conclusion, the obtainment of only one isomer of **1** and **2** from a Z/E mixture of 2-(trimethylsilyl)vinyl bromide **3** shows the high stereoselectivity of the coupling reaction. This feature can be used for the synthesis of polyfunctionalized vinyl phosphonates possessing a definite stereochemistry. Furthermore, the presence of a vinyl silane[12] as well as a vinyl phosphonate moiety in **1** and **2** should make those compounds useful synthons. Their use in the Diels Alder reaction gives adducts with potentialities in synthesis.

EXPERIMENTAL

2-(trimethylsilyl)vinyl bromide **3** was purchased from Fluka as a ca. 90/10 mixture of E and Z isomers. It can alternatively be synthesized from trimethylsilyl acetylene[14] to give the same mixture. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$, on a Bruker AC 100 spectrometer at 100.00 MHz and 25.18 MHz, respectively (the usual abbreviations are used: s = singulet, d = doublet, t = triplet, q = quadruplet, m = multiplet). ^{31}P NMR spectra were recorded at 40.54 MHz. The positive chemical shift values are downfield from Me_4Si (internal standard) for ^1H and ^{13}C spectra and 85% H_3PO_4 (external standard) for ^{31}P spectra. Endo and exo denominations refer to the phosphonyl group. Endo/exo ratios were determined by ^{31}P NMR and/or gas chromatographic analysis (SE-30 capillary column, 50 m, isotherm 160°C) of the crude adducts. Proton and carbon numbering refer to Equation 1 and Scheme I, respectively.

Dimethyl 2-(trimethylsilyl)vinyl phosphonate (**1**). Dimethyl phosphite (44 mmol), **3** (44 mmol), triethylamine (44 mmol), $Pd(PPh_3)_4$ (0.7 mmol) and toluene (15 mL) were mixed in a Pyrex Schlenk tube under a nitrogen atmosphere. The mixture was heated (50°C) on an oil bath with stirring. A white precipitate appeared and after 5 min., the mixture was allowed to cool to room temperature. It was diluted with ethyl acetate (50 mL), filtered, the solid was washed with ethyl acetate (100 mL), and the filtrate was reduced *in vacuo*. The residue was then purified by flash chromatography (silica, ether/ethyl acetate 3:1). Further Kugelrohr distillation (70°C/0.2 mm Hg, air bath temperature) afforded **1** as a colorless liquid in 80% yield.^1H NMR: 0.15 (s, Si—CH_3), 3.73 (d, CH_3O, $^3J_{PH}$ = 10.9 Hz), 6.22 (dd, H_2, $^2J_{PH}$ = 28.6 Hz, $^3J_{HH}$ = 20.7 Hz), 7.24 (dd, H_1, $^3J_{PH}$ = 34.6 Hz, $^3J_{HH}$ = 20.7 Hz); ^{13}C NMR: −2.08 (s, Si—CH_3), 52.36 (d, CH_3O, $^2J_{PC}$ = 6.0 Hz), 130.53 (d, =C—P, $^1J_{PC}$ = 175.5 Hz), 157.16 (d, =CH—Si, $^2J_{PC}$ = 4.5 Hz); ^{31}P NMR: 17.7 ppm.

Diethyl 2-(trimethylsilyl)vinyl phosphonate (**2**). was obtained by the same procedure as described above. Kugelrohr distillation (72°C/0.3 mm Hg, air bath temperature) afforded **2** as a colorless liquid in 76% yeld. ^{1}H NMR: 0.15 (s, Si—CH_3), 1.31 (t, CH_3, $^3J_{HH} = 7.0$ Hz), 4.21 (dt, CH_2O, $^3J_{HH} = 7.0$ Hz, $^3J_{PH} = 15.3$ Hz), 6.63 (dd, H_2, $^2J_{PH} = 27.1$ Hz, $^3J_{HH} = 20.6$ Hz), 7.65 (dd, H_1, $^3J_{PH} = 34.0$ Hz, $^3J_{HH} = 20.6$ Hz); ^{13}C NMR: −1.8 (s, Si—CH_3), 16.94 (d, CH_3, $^3J_{PC} = 5.8$ Hz), 91.83 (d, CH_2O, $^2J_{PC} = 5.8$ Hz), 134.73 (d, =C—P, $^1J_{PC} = 174.9$ Hz), 155.00 (d, =CH—Si, $^2J_{PC} = 3.8$ Hz); ^{31}P NMR: 15.56 ppm.

Dimethyl (3-trimethylsilyl 5-norbornen 2-yl) phosphonate (**4a/4b**). To a cooled (0°C) suspension of $AlCl_3$ (10 mmol) in dichloromethane (5 ml) was added with stirring a solution of **1** (10 mmol) in dichloromethane (5 mL). Freshly distilled cyclopentadiene (3 mL, 4 equiv.) was added dropwise after 10 min., and the mixture was allowed to attain room temperature with stirring. After 24 hours, the reaction mixture was quenched with satd. ammonium chloride, extracted twice with dichloromethane, and the combined organic layers were dried over anhydrous $MgSO_4$. Removal of solvent *in vacuo* left a yellowish liquid which was purified by Kugelrohr distillation (110°C/0.02 mm Hg, air bath temperature) to give a colorless oil. Compounds **4a/4b** were further separated by column chromatography (silica, ether).

(**4a**): ^{1}H NMR: 0.10 (s, Si—CH_3), 0.79 (ddd, H_3, $^3J_{PH} = 21.6$ Hz, $^3J_{H2H3} = 6.9$ Hz, $^3J_{H3H4} = 1.7$ Hz), 1.13–1.32 (m, 2H, H_7), 2.27 (ddd, H_2, $^2J_{PH} = 14.2$ Hz, $^3J_{H2H3} = 6.9$ Hz, $^3J_{H1H2} = 3.1$ Hz), 2.88 (broad s, H_4), 3.25 (broad s, H_1), 3.66 and 3.73 (d, CH_3O, $^3J_{PH} = 4.3$ Hz), 6.06 (dd, H_6, $^3J_{H5H6} = 5.4$ Hz, $^3J_{H1H6} = 2.9$ Hz), 6.32 (dd, H_5, $^3J_{H5H6} = 5.4$ Hz, $^3J_{H4H5} = 3.0$ Hz); ^{13}C NMR: −1.64 (s, Si—CH_3), 28.28 (d, C_3, $^2J_{PC} = 2.0$ Hz), 37.78 (d, C_2, $^1J_{PC} = 150.5$ Hz), 44.52 (d, C_4, $^3J_{PC} = 7.5$ Hz), 45.55 (d, C_1, $^2J_{PC} = 1.8$ Hz), 48.61 (d, C_7, $^3J_{PC} = 16.6$ Hz), 51.96 and 52.24 (d, CH_3O, $^2J_{PC} = 5.5$ Hz), 131.73 (d, C_6,$^3J_{PC} = 4.7$ Hz), 138.91 (s, C_5); ^{31}P NMR: 35.21 ppm. (**4b**): ^{1}H NMR: −0.10 (s, Si—CH_3), 1.07–1.63 (complex m, 4H, H_2, H_3, H_7), 3.05 (broad s, 2H, H_1, H_4), 3.60 and 3.82 (d, CH_3O, $^2J_{PH} = 3.6$ Hz), 6.00 (broad s, 2H, H_5, H_6); ^{13}C NMR: −2.18 (s, Si—CH_3), 26.38 (s, C_3), 36.15 (d, C_2, $^1J_{PC} = 139.3$ Hz), 43.78 (s, C_4), 44.61 (d, C_1, $^2J_{PC} = 3.3$ Hz), 47.89 (s, C_7), 51.31 and 52.11 (d, CH_3O, $^2J_{PC} = 8.8$ Hz), 134.94 (d, C_6, $^3J_{PC} = 9.3$ Hz), 135.37 (s, C_5); ^{31}P NMR: 36.11 ppm.

Diethyl (3-trimethylsilyl 5-norbornen 2-yl) phosphonate (**5a/5b**). The same procedure as described above led to a colorless oil after Kugelrohr distillation (100°C/0.005 mm Hg, air bath temperature). **5a** and **5b** were further separated by column chromatography (silica, ether/ethyl acetate, 95:5).

(**5a**): ^{1}H NMR: 0.07 (s, Si—CH_3), 0.75 (ddd, H_3, $^3J_{PH} = 21.5$ Hz, $^3J_{H2H3} = 6.9$ Hz, $^3J_{H3H4} = 1.6$ Hz), 1.30 (dt, 8H, $C\underline{H}_3CH_2O$, $^3J_{HH} = 7.1$ Hz, $^4J_{PH} = 3.0$ Hz, and H_7), 2.24 (ddd, H_2, $^2J_{PH} = 14.3$ Hz, $^3J_{H2H3} = 6.9$ Hz, $^3J_{H1H2} = 3.1$ Hz), 2.85 (broad s, H_4), 3.23 (broad s, H_1), 4.05 (dq, CH_2O, $^3J_{HH} = 7.1$ Hz, $^3J_{PH} = 3.1$ Hz), 6.04 (dd, H_6, $^3J_{H5H6} = 5.5$ Hz, $^3J_{H1H6} = 2.8$ Hz), 6.28 (dd, H_5 $^3J_{H5H6} = 5.5$ Hz, $^3J_{H4H5} = 3.1$ Hz); ^{13}C NMR: −1.90 (s, Si—CH_3), 16.28 (d, $\underline{C}H_3CH_2O$, $^3J_{PC} = 3.8$ Hz), 27.84 (d, C_3, $^2J_{PC} = 2.4$ Hz), 37.86 (d, C_2 $^1J_{PC} = 151.0$ Hz), 44.21 (d, C_4, $^3J_{PC} = 7.6$ Hz), 45.22 (d, C_1, $^2J_{PC} = 2.1$ Hz), 48.24 (d, C_7, $^3J_{PC} = 16.9$ Hz), 60.50 and 60.84 (d, CH_2O, $^2J_{PC} = 7.2$ Hz), 131.45 (d, C_6, $^3J_{PC} = 4.9$ Hz), 138.28 (s, C_5); ^{31}P NMR: 32.72 ppm. (**5b**): ^{1}H NMR: −0.08 (s, Si—CH_3), 1.28 (dt, $C\underline{H}_3CH_2O$, $^3J_{HH} = 7.0$ Hz, $^4J_{PH} = 2.5$ Hz), 1.44–1.67 (complex m, 4H, H_2, H_3, H_7), 2.98 (broad s, 2H, H_1, H_4), 4.07 (dq, CH_2O, $^3J_{HH} = 7.0$ Hz, $^3J_{PH} = 4.0$ Hz), 6.03 (broad s, 2H, H_5, H_6); ^{13}C NMR: −1.18 (s, Si—CH_3), 16.43 (d, $\underline{C}H_3CH_2O$, $^3J_{PC} = 3.3$ Hz), 27.24 (s, C_3), 37.53 (d, C_2, $^1J_{PC} = 139.2$ Hz), 44.71 (s, C_4), 45.50 (d, C_1, $^2J_{PC} = 3.4$ Hz), 48.69 (s, C_7), 61.08 and 61.54 (d, CH_2O, $^2J_{PC} = 7.1$ Hz), 136.04 (s, C_5), 136.08 (d, C_6, $^3J_{PC} = 10.6$ Hz), ^{31}P NMR: 33.85 ppm.

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