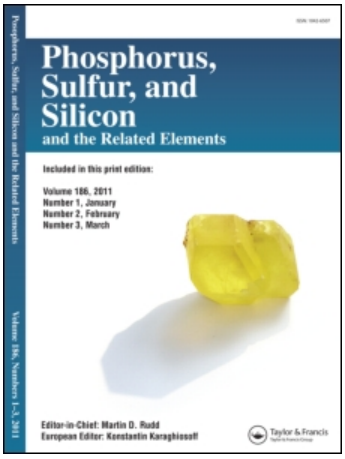

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

The Stereoselective Synthesis of Conjugated Allylsilanes

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To cite this Article Mahran, Mohamed Refat H. , Yosef, Hisham Abdallah A. and Effenberger, Franz(2006) 'The Stereoselective Synthesis of Conjugated Allylsilanes', Phosphorus, Sulfur, and Silicon and the Related Elements, 181: 10, 2283 — 2295

To link to this Article: DOI: 10.1080/10426500600616589

URL: http://dx.doi.org/10.1080/10426500600616589

Phosphorus, Sulfur, and Silicon, 181:2283–2295, 2006

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500600616589

Taylor & Francis
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The Stereoselective Synthesis of Conjugated Allylsilanes

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*2-trimethylsilylethylidenetriphenylphosphorane (**5**) (Seyferth–Wittig reagent) reacts stereoselectively with the carbonyl compounds **6a–f** to give the conjugated allylsilanes **7a–f**, each as a mixture of E-and Z-isomers. The stereoselectivity of reactions of E-cinnamaldehyde (**6c**) with **5** has been investigated at different temperatures. A successful E-stereoselective synthesis of **7c** was achieved by reacting **5** with E-cinnamaldehyde (**6c**) under the conditions of a Wittig–Schlosser modification reaction. Structures of the allylsilanes **7a–f** were deduced by compatible analytical and spectroscopic (IR, ^{1}H NMR, ^{13}C NMR, and GC/MS) measurements. An assignment of the E:Z ratios of **7a–f** is based on their ^{1}H NMR spectral data.*

Keywords Allylsilanes; Seyferth–Wittig reagents; structure elucidation; Wittig–Schlosser modification

INTRODUCTION

Since allylsilanes hold a tremendous potential as reagents and intermediates in the field of preparative organic chemistry,[2,3] there has been a relentless and continuing search for methods[4–8] for the preparation of a diverse range of simple and functionalized allylsilanes. A

Received September 15, 2005; accepted January 19, 2006.
This work is considered as "Organophosphorus Chemistry 35" for part 34. cf. ref. 1.
H. A. A. Yosef is grateful to the German Academic Exchange Service for the award of a fellowship, and M. R. H. Mahran is profoundly indebted to the Alexander von Humboldt-Stiftung (Federal Republic of Germany) for the generous donation of HPLC Equipment (Perkin-Elmer, system 1022, model 135 C).
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relatively straightforward synthetic route to a wide variety of allylsilanes is the Wittig reaction of 2-silyl phosphorus ylides with carbonyl compounds,[4,5,9] which was introduced by Seyferth et al.[4] and then modified by Fleming and Paterson.[5] The stereoselectivity of the reaction and subsequently the stereochemistry of the alkenes prepared are highly influenced by the ylide structure, nature of the carbonyl reactant, and experimental conditions.[10–12]

Very few studies[9,13–15] have been devoted to the stereoselectivity of the Wittig reaction of 2-silylphosphoranes with carbonyl compounds. Some studies[16,17] have given a boost to the preparation of stereo-homogeneous allylsilanes for the stereoregulated synthesis of acyclic systems. In the present work, use is made of the Wittig–Schlosser modification[12,18–20] for the synthesis of stereochemically pure *E*-allylsilane derivatives.

RESULTS AND DISCUSSION

The Synthesis of the Conjugated Allylsilanes 7a–f via a Wittig Reaction

By following *Fleming's one-pot procedure*,[5] the conjugated carbonyl compounds **6a–f** with exclusive *E*-configuration were allowed to react with 2-trimethylsilylethylidenetriphenylphosphorane (**5**) to give the corresponding allylsilanes **7a–f** (Scheme 1). Combined GC/MS[21] measurements indicate that **7a–f** were isolated as mixtures of *E* and *Z* isomers. The *E:Z* ratios of compounds **7a–f** (Table I) were determined by a quantitative analysis of their ^{1}H NMR spectral data.[7,8,22] ^{1}H-^{1}H COSY NMR spectra of the new allylsilanes **7d–f** have provided helpful information to define the protons that belong to each isomer as well as to elucidate the connectivity of the carbon atoms to which the protons are attached for each individual isomer.[22] The IR frequencies[23] as well as the ^{13}C-NMR chemical shifts[24] of **7a–f** have also given valuable information in confirming their structures.

Table I summarizes the results of the synthesis of conjugated allylsilanes by a reaction of the corresponding aldehydes **6** with the reactive triphenylphosphorane **5**, following *Fleming's one-pot* procedure.

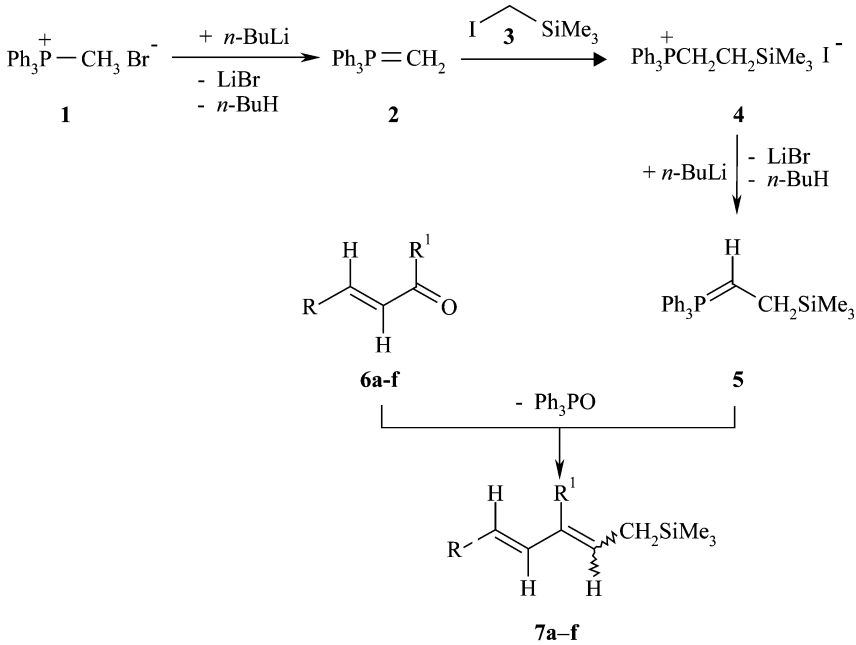
Z-selectivity occurs in the obtained allylsilanes **7a–d**. It is evident that **5** reacts with the unsaturated aldehydes **6a–d** to provide the allylsilanes **7a–d** with a higher proportion of *Z*-isomer (Table I) as expected in reactions of the un-stabilized triphenylphosphorus ylides (e.g., **5**) with aldehydes.[10,11,26] The *Z*-stereoselectivity is not very high, which may be attributable to the facile reversibility of the reactions with aromatic and α,β-unsaturated aldehydes.[27]

TABLE I Isomer Ratios and Yields of the Allylsilanes 7a–f

7	*E*:*Z* Ratio	Yield (%)
a	22:78	13.9[a]
b	33:67	29.8
c[b]	29:71	66.1
d	23:77	71.3
e	89:11	62.9
f	77:23	49.9

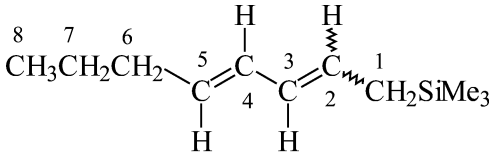
[a] The low yield may be attributed to the low b.p. and the loss during the chromatographic process and evaporation of eluent; cf. ref. 7 and 8.

[b] Cf. ref. 9 and 25.



6,7	a	b	c	d	e	f
R	H	CH_3	C_6H_5	*n*-C_3H_7	C_6H_5	
R[1]	H	H	H	H	CH_3	CH_3

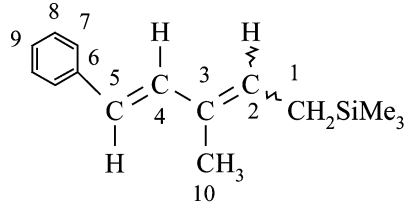
SCHEME 1



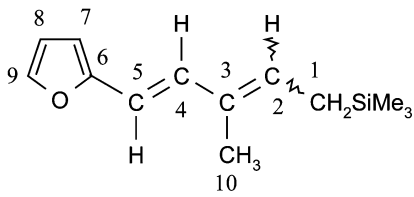
7d

SCHEME 2

Though compounds **7a,b** are known, they are now prepared for the first time by applying the Wittig reaction as a simple and direct substitute for other approaches, which are indirect ones.[7,8] Compound **7c** has been prepared previously also via a Wittig reaction by two different groups.[9,25] Ylide **5** reacts also with the conjugated ketones **6e,f** but with an inverted stereoselectivity compared to its reactions with aldehydes **6a–d** (Table I). The allylsilane **7d** is not yet described in the literature. Its structure is proved by GC/MS analysis, IR, as well as by ^{13}C and mainly ^{1}HNMR spectroscopy (see Experimental section). The methylene protons adjacent to the trimethylsilyl group of **7d** are expected to be deshielded when oriented *cis* (*Z*-isomer) to the C4-C5 double bond, due to its anisotropy, rather than when oriented *trans* (*E*-isomer).[7,8] Thus, they resonate in the ^{1}H NMR spectrum (using $CHCl_3$ as an internal standard) at $\delta = 1.49$ ppm (d, $J_{1-H,2-H} = 8.4$ Hz) for the *E*-isomer and at $\delta = 1.63$ ppm (d, $J_{1-H,2-H} = 8.9$ Hz) for the *Z*-isomer. Similarly, the two singlets at $\delta = 0.00$ and 0.01 ppm were attributed to the shielded CH_3-protons of $SiMe_3$ in the *E*- and *Z*-isomer, respectively. The doublet of triplets centered at $\delta = 5.35$ ppm is attributed to the C2-proton of the *Z*-isomer, while that of the *E*-isomer appears deshielded at $\delta = 5.48$ ppm due to the anisotropy of the C4-C5 double bond. This estimation is supported by the ^{1}H-^{1}H COSY NMR spectrum of **7d** wherein signals appearing at $\delta = 5.35$ and 5.48 ppm show cross peaks to the doublets that appeared at $\delta = 1.63$ and 1.49 ppm, respectively. The *E*:*Z*



7e



7f

SCHEME 3

ratio of 23:77 was confirmed also by an evaluation of the integral levels of the methylene protons adjacent to the trimethylsilyl group. As already mentioned, the dominant isomers of **7e** and **7f** are the *E*-isomers, which have the CH_2-$SiMe_3$ and CH_3 groups oriented *Z* to each other, exhibit *E:Z* ratios of 89:11 and 77:23, respectively (see spectral data in the Experimental section).

The *E:Z* ratio of allylsilane **7e**, taken as an example, was determined mainly *via* the ^{1}H NMR spectrum. It shows two singlets at $\delta = 0.00$ and 0.01 ppm ($CHCl_3$ as an internal standard) due to an absorption of the $SiMe_3$ protons of the *E*- and *Z*-isomer, respectively. The doublet centered at $\delta = 1.63$ ppm is attributed to the absorption of the methylene protons adjacent to the $SiMe_3$ group of the *E*-isomer, and the doublet centered at $\delta = 1.69$ ppm ($^3J_{1-H,2-H} = 9.8$ Hz) is attributed to the *Z*-isomer. Moreover, the olefinic proton C═CH─CH_2 is responsible for the two triplets appearing at $\delta = 5.49$ ($^3J_{2-H,1-H} = 9.8$ Hz) and 5.69 ppm ($^3J_{2-H,1-H} = 9.0$ Hz) belonging to the *Z*- and *E*-isomer, respectively.

The Temperature Dependence of the Reactions of Ylide 5 with E-Cinnamaldehyde (6c)

To investigate the effect of reaction conditions (e.g., temperature) on the stereoselectivity of the reactions with 2-silyl phosphorus ylides, *E*-cinnamaldehyde (**6c**) was reacted with 2-trimethylsilylethylidenetriphenylphosphorane (**5**) at different temperatures (Table II).

At −78°C the reaction was found to be *Z*-stereoselective yielding the allylsilane **7c** in an *E:Z* ratio of 29:71. When the THF solution of **6c** was added to **5** at 0°C, the reaction became nonstereoselective (an *E:Z* ratio of 48:52). A further increase of the reaction temperature had almost no effect any more (Table II).

For an incorporation of conjugated allylsilanes into self-assembled monolayers, we were mainly interested in the preparation of *all-E*

TABLE II Stereoselectivity of the Reaction of Ylide 5 With *E*-Cinnamaldehyde (6c) at Different Temperatures

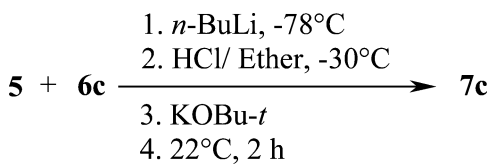
Reaction Temperature (°C)	Allylsilane 7c	
	E:Z(%)[a]	Yield%
−78	29:71	66.1
0	48:52	52.0
22	52:48	72.8
67	53:47	43.0

[a]E:Z ratios were determined from ^{1}H NMR data.

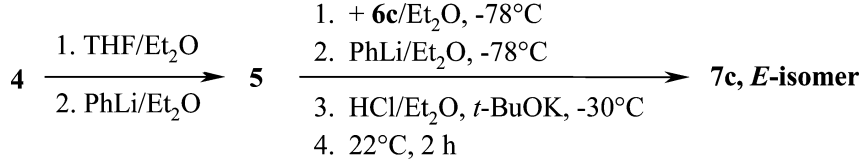
conjugated allylsilanes. We therefore investigated the Wittig–Schlosser modification of the olefination.

The *Trans*-Stereoselective Synthesis of a Conjugated Allylsilane by Applying A Wittig–Schlosser Modification

The stereochemical outcome of Wittig-reactions under various reaction conditions and strucural factors has been discussed and explained in many reports.[10,11,26,27] In an attempt to prepare an allylsilane with a predominant *E*-configuration, we have now applied the Wittig–Schlosser modification[12,18–20] on the reaction of ylide **5** with *E*-cinnamaldehyde (**6c**) at different reaction conditions (e.g., solvent and/or base) (Schemes 4 and 5).



SCHEME 4



SCHEME 5

In an attempt to optimize the *E*-isomer ratio of **7c**, reaction conditions described by Schlosser et al.[18,20] and Schlosser and Christmann[19] have been followed. Thus, 2-trimethylsilylethyl-triphenylphosphonium iodide (**4**) was first prepared and isolated as described by Seyferth et al.[4] The treatment of a suspension of **4** in a 5:3 (v/v) solvent mixture of THF/Et_2O with phenyllithium/Et_2O[20] affords ylide **5**, which reacts in situ with **6c** (Scheme 5). After the usual workup, allylsilane **7c** was isolated in an *E:Z* ratio of 98:2 as determined from the ^{1}H-NMR spectrum. All ^{1}H and ^{13}CNMR signals that correspond to the *Z*-isomer have almost disappeared.

CONCLUSION

From the results presented, it could be demonstrated that the reaction of 2-silyl phosphorus ylides (e.g., **5**) with conjugated carbonyl compounds (e.g., **6a–f**) can be successfully applied for the synthesis of conjugated allylsilanes (e.g., **7a–f**). This approach contributes highly to the synthetic potential of the Wittig reactions since allylsilanes are very useful reagents and intermediates in the field of synthetic organic chemistry.[2,3] The reactions of ylide **5** with the carbonyl compounds **6a–f** following *Fleming's one-pot procedure* were found to be nonstereoselective at r.t. and becoming more *Z*-selective at lower temperatures. The Wittig–Schlosser modification, however, can be applied successfully in the reaction of 2-silyl phosphorus ylides (e.g., **5**) with aldehydes (e.g., **6c**) in order to prepare stereoselectively almost pure *E*-allylsilanes. Applying the experimental conditions described by Schlosser using a self-prepared phenyllithium containing soluble lithium bromide resulted in an almost exclusive formation of *all-E* **7c**.

EXPERIMENTAL

All reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen or argon. Solvents were rigorously dried: diethyl ether and THF by distillation from sodium in the presence of benzophenone (sodium diphenylketyl) under an atmosphere of dry nitrogen, and petroleum ether by fractional distillation. Standard syringe techniques were applied for the transfer of bases and dry solvents as well as solutions of the reacting carbonyl compounds. Reacting aldehydes **6a–d** were distilled directly before use. Carbonyl compounds **6b–f** were pure *E*-isomers (^{1}H and ^{13}C NMR spectra). Isolated allylsilanes **7a–f** were stored at -15°C. Pure compounds were isolated by liquid chromatography using columns with different sizes packed with silica gel 60 (0.040–0.063 mm) (Merck) after an elution with the appropriate solvent. Infrared spectra were obtained from $CDCl_3$ solutions using a Perkin Elmer Printer 283 spectrophotometer and are reported in cm^{-1}. ^{1}H NMR spectra as well as ^{1}H-^{1}H COSY NMR spectra were measured using a Brucker AC 250F spectrometer operating at 250 MHz. Proton chemical shifts (δ) are reported in ppm downfield from TMS; $CDCl_3$ was used as a solvent and $CHCl_3$ as an internal standard at $\delta = 7.25$ ppm downfield from TMS. ^{13}C NMR spectra were recorded on a Bruker AC 250F instrument operating at 63 MHz. Chemical shifts (δ) are given in ppm downfield from TMS and referenced to the central peak of $CDCl_3$ at $\delta = 77.0$ ppm. Mass spectra were recorded with a Finnigan 4500 GC/MS spectrometer at 70 eV. Gas-liquid chromatography and HPLC

were used for purity control and the detection of geometrical isomers using Hewlett Packard 5700A and Hewlett Packard 5890 seriesII with autoinjector 7673 instruments. MS measurements were carried out using electron impact ionization (electron energy = 70 eV) for compounds **7a**,**d**,**e** or chemical ionization using methane as a reactant gas for compounds **7b**,**c**,**f**.

The Synthesis of the Conjugated Allylsilanes 7a–f via a Wittig Reaction: General Procedure[5]

n-BuLi (1.6 molar solution in hexane) was added dropwise with stirring over 0.5 h to a suspension of methyltriphenylphosphonium bromide (**1**) in abs. THF at 0°C under dry nitrogen. The ice bath was removed, and the mixture was warmed to r.t. (ca. 0.5 h) and stirred for 1 h to give a yellow solution of methylenetriphenylphosphorane (**2**). The reaction mixture was recooled to 0°C, and iodomethyltrimethylsilane (**3**) was added over 10 min. The mixture was allowed again to come slowly to r.t. (ca. 0.5 h) when 2-trimethylsilylethyltriphenylphosphonium iodide (**4**) precipitated. After 1 h, the reaction mixture was treated with a second mole equivalent of *n*-BuLi at −78°C. The cooling bath was removed, and the mixture was allowed to warm slowly to r.t. (ca. 1 h) and stirred for a further 1.5 h to give a dark red solution of 2-trimethylsilylethylidenetriphenyl-phosphorane (**5**). The carbonyl compound **6** in abs. THF was then added dropwise over 15 min to the ylide solution at –78°C under nitrogen. After 0.5 h, the cooling bath was removed, and the reaction mixture was allowed to warm slowly to r.t., and stirred under nitrogen for 16 h, quenched by pouring onto saturated ammonium chloride solution and extracted with diethyl ether. The organic extract was dried ($MgSO_4$) and evaporated in vacuo. Allylsilanes **7a–f** were isolated by column chromatography on silica gel after an elution with CCl_4 for **7a**,**b** and with petroleum ether for **7c–f** (Table III). The experimental data for the synthesis of the allylsilanes **7a–f** are summarized in Table III.

1-(Trimethylsilylmethyl)-4-propyl-1,3-butadiene (7d)

Colorless oil (1.30 g, 71.3%; *E*:*Z* 23:77). Calcd. for $C_{11}H_{22}Si$ (182.38): C, 72.44; H, 12.16. Found: C, 72.30; H, 12.27. IR ($CDCl_3$, cm^{-1}): 3000 (m, ν =C–H alkene); 2940 (vs, ν_{as} CH_3); 2905 (s, ν_{as} CH_2); 2880 (s, ν_s CH_3); 2855 (s, ν_s CH_2); 1595 (w, ν C=C alkene); 1410 (w, δ_{as} CH_3 on Si); 1235 (s, δ_s CH_3 on Si); 970 (s, δ CH=CH *trans* out-of-plane def.); 840 (vs), 760 (w) (CH_3 on Si rocking vib.); 650 (w, ν_{as} Si–C); 580 (w, ν_s Si–C).

^{1}H NMR ($CDCl_3$, δ): 0.00 [s, 9H, Si(C$\underline{H_3}$)$_3$, *E*-isomer]; 0.01 [s, 9H, Si(C$\underline{H_3}$)$_3$, *Z*-isomer]; 0.89 [t, $^3J_{8,7}$ = 7.3 Hz, 3H, 8-H, *E*-isomer]; 0.90

TABLE III The Synthesis of Allylsilanes 7a–f by Reacting Ylide 5 With Carbonyl Compounds 6a–f

1a (g/mmol)	THF (mL)	*n*-BuLi (mL/mmol)	**3** (g/mmol)	**6**/THF (g/mmol)/(mL)	NH_4Cl. sol(mL)	Et_2O (mL)	Allylsilane **7**	R_f (Eluent)	*E:Z*
8.03/22.5	40	15.6/25	4.82/22.5	**6a** (1.12/20)/10	100	3 × 300	**7a** Colorless liquid		22:78
8.03/22.5	40	15.6/25	4.82/22.5	**6b** (1.4/20)/10	100	3 × 300	**7b** Colorless oil		33:67
8.03/22.5	40	15.6/25	4.82/22.5	**6c** (2.64/20)/10	100	3 × 300	**7c** Colorless oil		29:71
4.02/11.25	20	7.8/12.5	2.41/11.25	**6d** (0.98/10)/5	50	3 × 150	**7d** Colorless oil	0.77 Pet. ether (40–60°)	23:77
8.03/22.5	40	15.6/25	4.82/22.5	**6e** (2.92/20)/10	100	3 × 300	**7e** White waxy solid	0.56 Pet. ether (60–80°)	89:11
4.02/11.25	20	7.8/12.5	2.41/11.25	**6f** (1.36/10)/5	50	3 × 150	**7f** Yellow oil	0.48 Pet. ether (60–80°)	77:23

[t, $^3J_{8,7}$ = 7.3 Hz, 3H, 8-H, *Z*-isomer]; 1.32–1.46 [m, 4H, 7-H, *E*- and *Z*-isomers]; 1.49 [d, $^3J_{1,2}$ = 8.4 Hz, 2H, 1-H, *E*-isomer]; 1.63 [d, $^3J_{1,2}$ = 8.9 Hz, 2H, 1-H, *Z*-isomer]; 1.98–2.11 [m, 4H, 6-H, *E*- and *Z*-isomers]; 5.35 [dt, $^3J_{2,1}$ = 8.9 Hz, $^3J_{2,3}$ = 10.8 Hz, 1H, 2-H, *Z*-isomer]; 5.48 [dt, $^3J_{2,1}$ = 8.4 Hz, $^3J_{2,3}$ = 13.6 Hz, 1H, 2-H, *E*-isomer]; 5.56 [dt, $^3J_{5,4}$ = 14.6 Hz, $^3J_{5,6}$ = 7.6 Hz, 1H, 5-H, *E*-isomer]; 5.60 [dt, $^3J_{5,4}$ = 15.0 Hz, $^3J_{5,6}$ = 7.0 Hz, 1H, 5-H, *Z*-isomer]; 5.87 [dd, $^3J_{3,2}$ = 13.6 Hz, $^3J_{3,4}$ = 10.1 Hz, 1H, 3-H, *E*-isomer]; 5.89 [t, $^3J_{3,2}$ = 10.8 Hz, 1H, 3-H, *Z*-isomer); 5.99 [dd, $^3J_{4,3}$ = 10.1 Hz, $^3J_{4,5}$ = 14.6 Hz, 1H, 4-H, *E*-isomer); 6.24 [dd, $^3J_{4,3}$ = 11.0 Hz, $^3J_{4,5}$ = 15.0 Hz, 1H, 4-H, *Z*-isomer).

^{13}C NMR ($CDCl_3$,δ): −1.9 [Si($\underline{C}H_3)_3$, *E*-isomer]; -1.7 [Si($\underline{C}H_3)_3$, *Z*-isomer]; 12.7 [C8, *E*-isomer]; 13.7 [C8, *Z*-isomer]; 19.3 [C1, *Z*-isomer]; 19.8 (C7, *E*-isomer); 22.7 (C7, Z-isomer); 23.4 (C1, *E*-isomer); 34.8 [C6, *E*-isomer); 35.0 (C6, *Z*-isomer); 126.0, 126.2, 126.5, 128.8, 129.3, 130.3, 130.8, 133.0 (C2, C3, C4, C5, *E*− and *Z*-isomers).

GC/EIMS [70 eV, m/z (relative abundance %)], *E*-isomer: 182 (1.8) $[M]^+$, 109 (< 1) $[M - SiMe_3]^+$, 108 (2.4) $[M - (SiMe_3 + H)]^+$, 73 (100) $[SiMe_3]^+$; *Z*-isomer: 182 (2.6) $[M]^+$, 109 (<1) $[M - SiMe_3]^+$, 108 (2.6) $[M - (SiMe_3 + H]^+$, 73 (100) $[SiMe_3]^+$.

1-(Trimethylsilylmethyl)-2-methyl-4-phenyl-1,3-butadiene (7e).

White waxy solid (2.90 g, 62.9%; *E*:*Z* 89:11), m.p. 32–34°C. Calcd. for $C_{15}H_{22}Si$ (230.42): C, 78.19; H, 9.62. Found: C, 78.18; H, 9.77. IR ($CDCl_3$, cm^{-1}): 3060 (w), 3040 (w) (ν =C=H arom); 3010 (m, ν =C−H alkene); 2940 (s, ν_{as} C−H satd.); 2870 (m, ν_s C−H satd.); 1620 (m, ν C=C alkene); 1590 (m), 1485 (m) (ν C=C arom); 1405 (w, δ_{as} CH_3 on Si); 1240 (s, δ_s CH_3 on Si); 945 (s, δ CH=CH *trans* out-of-plane def.); 840 (vs), 765 (w) (CH_3 on Si rocking vib.); 650 (w, ν_{as} Si−C); 595 (w, ν_s Si−C);

^{1}H NMR ($CDCl_3$, δ): 0.00 [s, 9H, Si($C\underline{H}_3)_3$, *E*-isomer]; 0.01 [s, 9H, $Si(CH_3)_3$, *Z*-isomer]; 1.63 [d, $^3J_{1,2}$=9.0 Hz, 2H, 1-H, *E*-isomer]; 1.69 [d, $^3J_{1,2}$ = 9.8 Hz, 2H, 1-H, *Z*-isomer]; 1.78 [d, $^4J_{6,2}$ = 0.6 Hz, 3H, 6-H, *E*-isomer]; 1.91 [d, $^4J_{6,2}$ = 1.1 Hz, 3H, 6-H, *Z*-isomer]; 5.49 [t, $^3J_{2,1}$ = 9.8 Hz, 1H, 2-H, *Z*-isomer]; 5.69 [t, $^3J_{2,1}$ = 9.0 Hz, 1H, 2-H, *E*-isomer]; 6.33 [d, $^3J_{5,4}$ = 16.0 Hz, 1H, 5-H, *E*-isomer]; 6.46 [d, $^3J_{5,4}$ = 16.0 Hz, 1H, 5-H, *Z*-isomer]; 6.79 [d, $^3J_{4,5}$ = 16.0 Hz, 1H, 4-H, *E*-isomer]; 7.08-7.37 [m, 11H, 4-H of *Z*-isomer and aromatic protons of *E*- and *Z*-isomers].

^{13}C NMR ($CDCl_3$, δ): –1.5 [$Si(CH_3)_3$, *E*- and *Z*-isomers); 12.4 [C10, *E*-isomer); 19.4 [C1, *Z*-isomer]; 20.4 [C10, *Z*-isomer]; 20.6 (C1, *E*-isomer); 124.0, 126.1, 126.4, 126.6, 127.0, 128.6, 131.3, 134.6 [C2, C4, C5, C7, C8, C9, *E*- and *Z*-isomers]; 129.8 (C3, *Z*-isomer); 131.7 [C3, *E*-isomer]; 138.4 (C6, *E*- and *Z*-isomers).

GC/EIMS [70 eV, m/z (relative abundance %)], *E*-isomer: 230 (4.1) $[M]^{+\cdot}$, 157 (<1) $[M\text{-}{}^{\cdot}SiMe_3]^+$, 156 (1.1) $[M\text{-}({}^{\cdot}SiMe_3 - {}^{\cdot}H]^{+\cdot}$, 143 (1.1) $[M - {}^{\cdot}CH_2SiMe_3]^+$, 73 (100) $[SiMe_3]^+$, *Z*-isomer: 230 (2.9) $[M]^{+\cdot}$, 157 (<1) $[M - {}^{\cdot}SiMe_3]^+$, 156 (<1) $[M - ({}^{\cdot}SiMe_3 - {}^{\cdot}H)]^{+\cdot}$, 143 (<1) $[M - {}^{\cdot}CH_2SiMe_3]^+$, 73 (100) $[SiMe_3]^+$.

1-(Trimethylsilylmethyl)-2-methyl-4-(2-furyl)-1,3-butadiene (7f)

Yellow oil (1.10 g, 49.9%; *E*:*Z* 77:23). Calcd. for $C_{13}H_{20}OSi$ (220.39): C, 70.85; H, 9.15. Found: C, 71.31; H, 9.21. IR ($CDCl_3$, cm^{-1}): 3100 (w, ν =C–H furan ring); 3030 (w, ν =C–H alkene); 2940 (m, ν_{as} C–H satd.); 2870 (w, ν_s C–H satd.); 1610 (m, ν C=C alkene); 1550 (w), 1480 (w) (ν C=C furan ring); 1405 (w, δ_{as} CH_3 on Si); 1240 (s, δ_s CH_3 on Si); 940 (s, δ CH=CH *trans*out-of-plane def.); 840 (vs), 775 (w) (CH_3 on Si rocking vib.); 650 (w, ν_{as} Si–C); 575 (w, ν_s Si–C).

^{1}H NMR ($CDCl_3$, δ): 0.00 [s, 9H, $Si(C\underline{H}_3)_3$, *E*-isomer]; 0.01 [s, 9H, $Si(CH_3)_3$, *Z*-isomer]; 1.63 [d, $^3J_{1,2} = 9.0$ Hz, 2H, 1-H, *E*-isomer]; 1.69 [d, $^3J_{1,2} = 9.2$ Hz, 2H, 1-H, *Z*-isomer]; 1.73 [d, $^4J_{10,2} = 0.5$ Hz, 3H, 10-H, *E*-isomer]; 1.86 [d, $^4J_{10,2} = 1.0$ Hz, 3H, 10-H, *Z*-isomer]; 5.49 [t, $^3J_{2,1} = 9.2$ Hz, 1H, 2-H, *Z*-isomer]; 5.7 [t, $^3J_{2,1} = 9.0$ Hz, 1H, 2-H, *E*-isomer]; 6.15 [d, $^3J_{5,4} = 16.0$ Hz, 1H, 5-H, *E*-isomer]; 6.16 [d, $^3J_{7,8} = 3.3$ Hz, 1H, 7-H, *E*-isomer]; 6.21 [d, $^3J_{7,8} = 3.5$ Hz, 1H, 7-H, *Z*-isomer]; 6.27 [d, $^3J_{5,4} = 15.9$ Hz, 1H, 5-H, *Z*-isomer]; 6.34 [dd, $^3J_{8,7} = 3.3$ Hz, $^3J_{8,9} = 1.8$ Hz, 1H, 8-H, *E*-isomer]; 6.36 [dd, $^3J_{8,7} = 3.5$ Hz, $^3J_{8,9} = 1.6$ Hz, 1H, 8-H, *Z*-isomer]; 6.75 [d, $^3J_{4,5} = 16.0$ Hz, 1H, 4-H, *E*-isomer]; 7.04 [d, $^3J_{4,5} = 15.9$ Hz, 1H, 4-H, *Z*-isomer]; 7.29 [d, $^3J_{9,8} = 1.8$ Hz, 1H, 9-H, *E*-isomer]; 7.33 [d, $^3J_{9,8} = 1.6$ Hz, 1H, 9-H, *Z*-isomer].

^{13}C NMR ($CDCl_3$, δ): –1.58 [$Si(\underline{C}H_3)_3$, *Z*-isomer]; -1.55 [$Si(\underline{C}H_3)_3$, *E*-isomer]; 12.0 [C10, *E*-isomer]; 19.4 [C1, *Z*-isomer]; 20.3 [C10, *Z*-isomer]; 20.7 (C1, *E*-isomer); 106.4 (C7, *E*-isomer); 107.3 (C7, *Z*-isomer); 111.46 (C8, *E*-isomer); 111.52 (C8, *Z*-isomer); 112.3 [C5, *E*-isomer]; 115.1 [C5, *Z*-isomer]; 129.4 [C3, *Z*-isomer]; 131.3 (C3, *E*-isomer); 125.0, 129.0, 131.5, 133.3 (C2, C4, *E*- and *Z*-isomers); 141.2 (C9, *E*-isomer); 141.6 (C9, *Z*-isomer); 154.3 (C6, *E*- and *Z*-isomers).

GC/EIMS [70 eV, m/z (relative abundance %)], *E*-isomer: 221 (100) $[MH]^+$, 220 (74.2) $[M]^{+\cdot}$, 205 (63.9) $[M - {}^{\cdot}CH_3]^+$, 147 (5.2) $[M - {}^{\cdot}SiMe_3]^+$, 73 (29.9) $[SiMe_3]^+$, *Z*-isomer: 221 (100) $[MH]^+$; 220 (92.6) $[M]^{+\cdot}$, 205 (96.8) $[M - {}^{\cdot}CH_3]^+$, 147 (4.2) $[M - {}^{\cdot}SiMe_3]^+$, 73 (32.6) $[SiMe_3]^+$.

The Synthesis of *all-E* Allylsilane 7c by Applying the Schlosser Modification of the Wittig Reaction

Starting from Methyltriphenylphosphonium Bromide (1)

Ylide **5** was prepared as described in the general procedure from **1** (4.02 g, 11.25 mmol), *n*-BuLi (7.8 mL, 12.5 mmol), and **3** (2.41 g, 11.25

mmol) in THF (20 mL). Then a solution of *E*-cinnamaldehyde (**6c**) (1.32 g, 10 mmol) in abs. THF (5 mL) was added to the ylide solution at −78°C within 5 min under a dry N_2 atmosphere. After decoloration of the reaction mixture (5 min), an additional amount of *n*-BuLi (6.3 mL of 1.6 molar solution in hexane, 10 mmol) was added at – 78°C to give the dark red solution of the β-oxidophosphonium ylide (betaine ylide). The reaction mixture was vigorously stirred while the temperature was being raised gradually to −35°C (25 min), then ethereal HCl (11 mL of 1*N* HCl in 20 mL of diethyl ether) was added, causing an immediate decolouration. After an addition of potassium *tert*-butoxide (1.7 g, 15 mmol), the mixture was allowed to warm slowly to r.t., stirred for further 2 h, quenched by pouring onto saturated ammonium chloride solution (50 mL), and extracted with diethyl ether (3 × 150 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated in *vacuo*. The residue was chromatographed on silica gel with petroleum ether to give the allylsilane **7c** in a 47.6% yield, and the *E*:*Z* ratio = 72:28.

Starting from 2-trimethylsilylethyltriphenylphosphonium Iodide (4)

Phenyllithium (4 mL of 1.5 molar solution, 6 mmol) in Et_2O was added dropwise with stirring over 0.5 h to a suspension of 2-trimethylsilyl-ethyltriphenylphosphonium iodide (**4**),[4] prepared by reacting iodo-methyltrimethylsilane (**3**) with a freshly prepared solution of methylene-triphenylphosphorane (**2**)[28] (2.9 g, 6 mmol) in a solvent mixture of abs. THF (10 mL) and abs. diethyl ether (6 mL) at −78°C under dry nitrogen. The mixture was allowed to warm slowly to r.t. (1 h) and stirred for further 2 h to give the dark red-colored solution of 2-trimethylsilyl-ethylidenetriphenylphosphorane (**5**). The reaction mixture was cooled again to −78°C, and a solution of *E*-cinnamaldehyde (**6c**) (0.8 g, 6 mmol) in abs. diethyl ether (3 mL) was added over 2 min. After decolouration of the reaction mixture (5 min), an additional mole equivalent of PhLi (4 mL of 1.5 molar solution, 6 mmol) was added at −78°C to give the dark red solution of β-oxidophosphonium ylide (betaine ylide). The reaction mixture was vigorously stirred while the temperature was raised gradually to −35°C (25 min), then ethereal HCl (7 mL of *1N* HCl in 15 mL of Et_2O) was added causing an immediate decolouration. After an addition of potassium *tert*-butoxide (1.01 g, 9 mmol), the mixture was allowed to warm slowly to r.t. and then stirred for a further 2 h, quenched by pouring onto saturated ammonium chloride solution (30 mL) and extracted with diethyl ether (3 × 100 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated *in vacuo*. The residue was chromatographed on silica gel with petroleum

ether to give the allylsilane **7c** as almost exclusively the *E*-isomer (*E:Z* ratio = 98:2) in a 42.4 % yield.

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