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A Practical Procedure for the Preparation of (1*E*,3*E*)-5-Alkoxy-1-siloxy-1,3-dienes

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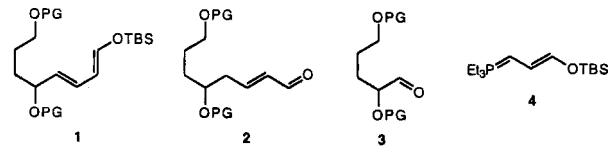
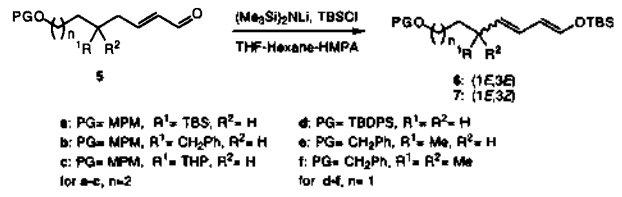
Siloxydienes have been widely used in organic synthesis. They are known to take a variety of electrophiles in the presence of Lewis acid or fluoride anion.[1] They are also finding widespread use in Diels-Alder reactions.[2] During studies related with substituent effects on the stereo- and regiochemical outcome of Diels-Alder reaction, we needed to prepare various (1*E*,3*E*)-5-alkoxy-1-siloxy-1,3-dienes such as **1**. Generally, 1-siloxy-1,3-dienes have been prepared from α,β-unsaturated aldehydes by deprotonation of the γ-position followed by trapping of the resulting anions with the silylating agents.[1d,2c] Unfortunately, these methods do not work well with δ-alkoxy-α,β-unsaturated aldehydes such as **2**.[3] Elimination of the δ-alkoxy group is known to be a serious obstacle to access to desired dienes. Such difficulties can be removed by employing the Wittig process, for example, by reacting α-alkoxyaldehydes **3** with phosphoranes **4**.[3,4] However, the stereoselectivities which attend such procedure are not satisfactory (ratios of 1*E*,3*E*-dienes to other dienes are ~2 : 1). Thus, the development of a more practical and stereoselective procedure for the preparation of (1*E*,3*E*)-5-alkoxy-1-siloxy-1,3-dienes is of value.



We have examined the preparation of (1*E*,3*E*)-5-alkoxy-1-siloxy-1,3-dienes from δ-alkoxy-α,β-unsaturated aldehydes, in hopes that achievement of simultaneous deprotonation and enolate trapping could minimize the elimination of the δ-alkoxy group. It was also anticipated that at low temperatures, kinetic deprotonation would occur with maintenance of the initially preferred transoid relationship between the C=O group[5] and the C=C bond to secure the *E*-stereochemistry of the siloxy-containing double bond.

Upon surveying reaction conditions using δ-*t*-butyldimethylsilyloxy-α,β-unsaturated aldehyde **5a** as a model substrate, it was found that treatment of the enal **5a** with lithium bis(trimethylsilyl)amide in the presence of *t*-butyldimethylsilyl chloride in tetrahydrofuran-hexane containing hexamethylphosphoramide (~5 : 1 THF-Hexane/HMPA) at



Scheme 1.

Table 1. Preparation of 1-Siloxydienes by Treatment of Enals with $(Me_3Si)_2NLi$ and TBSCl in THF-Hexane-HMPA at -78 °C

Entry	Enal	Siloxy-diene	Ratio	Yield* (%)
1	**5a**	**6a/7a**	>95 : 5	83
2	**5b**	**6b/7b**	>95 : 5	86
3	**5c**	**6c/7c**	>95 : 5	81
4	**5d**	**6d/7d**	1 : 2.5	92
5	**5e**	**6e/7e**	~1 : 1	85
6	**5f**	**6f/7f**	>10:1	77

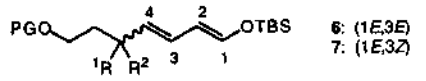
*Yields refer to isolated yields of products purified by chromatography

-78 °C gave (1*E*,3*E*)-5-*t*-butyldimethylsilyloxy-1-siloxy-1,3-diene **6a** with the selectivity of higher than 95 : 5 in high yield (Scheme 1).[6] The choice of lithium bis(trimethylsilyl) amide as a base was important to the success of the reaction. When other bases such as lithium diisopropylamide (LDA) were used, either conversion was low or serious elimination of the δ-*t*-butyldimethylsilyloxy group was observed. The use of HMPA as a cosolvent was also crucial. Without HMPA, the conversion was very poor at -78 °C and the slow elevation of the reaction temperature caused the elimination of the δ-*t*-butyl-dimethylsilyloxy group to give the α,β,γ,δ-unsaturated aldehyde as the major product.

As shown in Table 1, three δ-alkoxy-α,β-unsaturated aldehydes[7] (entry 1-3) could be transformed into the corresponding (1*E*,3*E*)-5-alkoxy-1-siloxy-1,3-dienes highly stereoselectively in high yields by this procedure. Basically, no significant amounts of other diene isomers were detected by high field ^{1}H NMR spectra. The stereochemistry at the double bonds of dienes **6a-c** was assigned on the basis of their ^{1}H coupling data (Table 2). The coupling constants of $J_{1,2}$=~11.5 Hz[8] and $J_{3,4}$=~15.4 Hz observed for **6a-c** indicated the *E,E*-stereochemistry of each diene. None of the dehydroalkoxylation product was detected in each case.

In order to see if the *E,E*-stereoselectivity is general in this deprotonative silylation process, we have employed this procedure to other enals **5d-f**[9] with no-, methyl-, and dimethyl substituents at the δ-position (Table 1, entry 4-6). In each case, a mixture of (1*E*,3*E*)- and (1*E*,3*Z*)-dienes was obtained. While the observed stereochemistry about the siloxy-containing double bonds was *E* as expected, the stereochemistry about the C-3 double bonds was dependent upon the substituent pattern at the C-5 position. When dimethyl groups are present (entry 6), a high degree of *E*-stereoselectivity (>10:1) was also achieved. However, no *E*-stereochemical preference was detected with C-5 methyl substituent (entry 5). And the reversal of the stereoselectivity was observed when no substituent was attached to the C-5 position of the enal system (entry 4). The results (entry 4, 5) were rather unexpected, considering the transition state structures shown in Figure 1. From the point of the steric interaction, the transition state A is favored over transition state B due to the $A^{1,3}$ interaction present in the transition state B. Thus, the *E*-stereoselectivity is expected even with **5d**. However, for some reasons, the Z-selectivity was observed. With bulkier R groups, as the nonbonded interaction in the transtion state B becomes bigger, the preference for the transition state A will be higher and thus the higher *E*-stereoselectivity is expected.

Table 2. ^{1}H NMR Data Important to the Stereochemical Assignment of 1-Siloxydienes



Diene	^{1}H NMR Data
6a[a]	H_1: d 6.50 (d, *J*=11.7 Hz, 1H);
	H_2: δ 5.66 (t, *J*=~11 Hz, 1H);
	H_3: δ 5.96 (dd, *J*=11.8, 15.4 Hz, 1H);
	H_4: δ 5.39 (dd, *J*=6.9, 15.4 Hz, 1H)
6b[a]	H_1: δ 6.56 (d, *J*=11.8 Hz, 1H);
	H_2: δ 5.72 (t, *J*=~11 Hz, 1H);
	H_3: δ 6.04 (dd, *J*=11.3, 15.3 Hz, 1H);
	H_4: δ 5.34 (dd, *J*=7.7, 15.3 Hz, 1H)
6c[a]	H_1: δ 6.50-6.54 (2d, *J*=11.5 Hz & *J*=12.1 Hz, 1H);
	H_2: δ 5.65-5.70 (2t, *J*=~11 Hz, each, 1H);
	H_3: δ 6.00-6.08 (2dd, *J*=10.4, 15.4 Hz, each , 1H);
	H_4: δ 5.47 (dd, *J*=7.1, 15.4 Hz, 0.5H) &
	δ 5.22 (dd, *J*=8.2, 15.4 Hz, 0.5H)
6d[b]	H_1: δ 6.45 (d, *J*=11.5 Hz, 1H); H_2: δ 5.96
	H_3: δ 5.66 (t, *J*=11.0 Hz, 1H);
	H_4: δ 5.42 (dd, *J*=7.1, 14.9 Hz, 1H)
7d[b]	H_1: δ 6.53 (d, *J*=11.5 Hz, 1H);
	H_2: δ 5.90 (t, *J*=11.5 Hz, 1H)
	H_3: δ 5.85 (dd, *J*=10.4, 11.5 Hz, 1H);
	H_4: δ 5.16 (m, J_{34}=10.4 Hz, 1H)
6e[b]	H_1: δ 6.46 (d, *J*=11.6 Hz, 1H);
	H_2: δ 5.65 (t, *J*=~11 Hz, 1H);
	H_3: δ 5.85; H_4: δ 5.30 (dd, *J*=8.2, 15.3 Hz, 1H)
7e[b]	H_1: δ 6.54 (d, *J*=11.6 Hz, 1H);
	H_2: δ 5.97 (t, *J*=11.6 Hz, 1H);
	H_3: δ 5.83; H_4: δ 4.95 (t, *J*=~11 Hz, 1H)
6f[b]	H_1: δ 6.49 (d, *J*=11.5 Hz, 1H);
	H_2: δ 5.72 (t, *J*=~11 Hz, 1H)
	H_3: δ 5.81 (dd, *J*=11.0, 15.4 Hz, 1H);
	H_4: δ 5.42 (d, *J*=15.4 Hz, 1H)

[a] 200 MHz NMR data. [b] 600 MHz NMR data

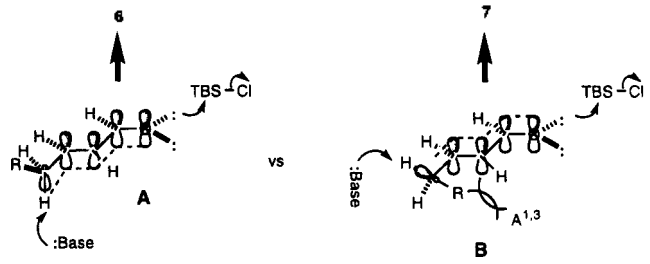


Figure 1. Possible Transition Structures Leading to **6** and **7**.

Although not all the substrates were examined, the stereoselectivity of the diene formation seemed to be sensitive to the the order of addition. For example, while the addition of an enal **5f** to a solution of $(Me_3Si)_2NLi$ and TBSCl in THF-HMPA gave a >10:1 mixture of (1*E*,3*E*)- and (1*E*,3*Z*)-dienes, the addition of $(Me_3Si)_2NLi$ to a solution of an enal **5f** and TBSCl in THF-HMPA gave a complex mixture of dienes in which (1*E*,3*E*)-diene **6f** and a diene with (1Z)-stereochemistry were present to the same degree and other dienes were also detected.

In summary, the present procedure of deprotonative silylation of δ-alkoxy enals offers a practical route to (1*E*,3*E*)-5-alkoxy-1-siloxy-1,3-dienes. This technique may also be of value in the preparation of (1*E*,3*E*)-5,5-dialkyl-1-siloxy-1,3-dienes.

Experimental

^{1}H NMR spectra were recorded on a Varian Gemini-200 (200 MHz) and a Varian Unity Plus-600 (600 MHz) spectrometer. The chemical shifts are reported in ppm from TMS with the solvent resonance as an internal standard ($CDCl_3$, 7.27 ppm). IR spectra were measured on MIDAC 101025 spectrometer. Tetrahydrofuran was distilled from sodium benzophenone ketyl. Methylene chloride was distilled from calcium hydride. All the chemicals were purchased from the Aldrich Chemical Co.

Preparation of (1*E*,3*E*)-1,5-di-*t*-butyldiemthylsilyloxy-1,3-diene 6a: General Procedure. To a solution of hexamethyldisilazane (252 μL, 1.22 mmol) in THF (1.5 mL) at 0 °C was added dropwise n-BuLi (1.46 M in hexane, 0.70 mL, 1.02 mmol). After being stirred at 0 °C for 45 min and at rt for 15 min, the mixture was cooled to − 78 °C and HMPA (0.80 mL) and TBSCl (1 M, 1.02 mL, 1.02 mmol) were added. A solution of the δ–*t*-butyldimethylsilyloxyenal **5a** (200 mg, 0.51 mmol) in THF (0.7 mL) was added dropwise and the mixture was stirred at this temperature for additional 20 min. Saturated sodium bicarbonate solution (~2 mL) was added dropwise and the mixture was warmed up to rt. The mixture was extracted with hexane (3×5 mL). The combined organic extracts were washed with brine (5 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by flash column chromatography (4% ethyl acetate in hexane, containing small amount of triethylamine) to give **6a** (214 mg, 83%) as a clear oil. IR (CCl_4) 2952, 2856, 1687, 1650, 1611, 1509, 1249, 1170, 1098 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.26 (d, *J*=8.5 Hz, 2H), 6.88 (d, *J*=8.5 Hz, 2H), 6.50 (d, *J* =11.7 Hz, 1H), 5.96 (dd, *J*=11.8, 15.4 Hz, 1H), 5.66 (t, *J*= ~11 Hz, 1H), 5.39 (dd, *J*=6.9, 15.4 Hz, 1H), 4.42 (s, 2H), 4.07 (m, 1H), 3.81 (s, 3H), 3.43 (t, *J*=6.6 Hz, 1H), 1.52-1,69 (m, 4H), 0.92 (s, 9H), 0.87 (s, 9H), 0.17 (s, 6H), 0.03 (s, 3H), 0.01 (s, 3H). By the same procedure for the preparation of **6a**, the following dienes were obtained. **6b**: IR (CCl_4) 3058, 3028, 2948, 2856, 1688, 1651, 1509, 1249, 1173, 1096 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.33 (m, 5H), 7.26 (d, *J*=8.0 Hz, 2H), 6.88 (d, *J*=8.0 Hz, 2H), 6.56 (d, *J*=11.8 Hz, 1H), 6.04 (dd, *J*=11.3, 15.3 Hz, 1H), 5.72 (t, *J*=~11 Hz, 1H), 5.34 (dd, *J*=7.7, 15.3 Hz, 1H), 4.54 (ABq, 2H), 4.41 (s, 2H), 3.81 (s, 3H), 3.71 (m, 1H), 3.42 (t, 2H), 1.59-1.75 (m, 4H), 0.94 (s, 9H), 0.17 (s, 6H). **6c**: 2936, 2856, 1687, 1651, 1610, 1509, 1248, 1174, 1113, 1034 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.26 (d, 2H), 6.88 (d, 2H), 6.50-6.54 (2d, *J*=11.5 Hz & *J*=12.1 Hz, 1H), 6.00-6.08 (2dd, *J*=10.4, 15.4 Hz, each , 1H), 5.65-5.70 (2t, *J*=~11 Hz, each, 1H), 5.47 (dd, *J*= 7.1, 15.4 Hz, 0.5H), 5.22 (dd, *J*=8.2, 15.4 Hz, 0.5H), 4.67 (m, 1H), 4.42 (s, 2H), 4.08 (m, 0.5H), 3.83 (m, 0.5H), 3.80 (s, 3H), 3.40-3.50 (m, 4H), 1.43-1.85 (m, 10H), 0.92 (s, 9H), 0.18 (s, 6H). **6d/7d**: IR (CCl_4) 3066, 2950, 2930, 2890, 1690, 1649, 1617, 1519, 1426, 1387, 1360, 1253, 1109 cm^{-1}; ^{1}H NMR ($CDCl_3$) d 7.62-7.69 & 7.34-7.46 (m, 10H), 6.53 (d, *J*=11.5 Hz, 0.7H), 6.45 (d, *J*=11.5 Hz, 0.3H), 5.96 (t, *J*= 11.5 Hz, 0.7H), 5.90 (m, 0.3H), 5.85 (dd, *J*=10.4, 11.5 Hz, 0.7H), 5.66 (t, *J*=11.0 Hz, 0.3H), 5.42 (dd, *J*=7.1, 14.9 Hz, 0.3H), 5.16 (m, J_{34}=10.4 Hz, 0.7H), 3.66 (t, 2H), 2.20 & 2.07 (2m, 2H), 1.62 (m, 2H), 1.03 (s, 9H), 0.90 (s, 9H), 0.18 (s, 6H). **6e/7e**: ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 5H), 6.54 (d, *J*=11.6 Hz, 0.5H), 6.46 (d, *J*=11.6 Hz, 0.5H), 5.97 (t, *J*= 11.6 Hz, 0.5H), 5.85 (0.5H), 5.83 (0.5H), 5.65 (t, *J*=~11 Hz, 0.5H), 5.30 (dd, *J*=8.2, 15.3 Hz, 0.5H), 4.95 (t, *J*=~11 Hz, 0.5H), 4.48 (2s, 2H), 3.45 (m, 2H), 3.2 (m, 1H), 2.70 (m, 0.5H), 2.32 (m, 0.5H), 1.70 (m, 0.5H), 1.63 (m, 0.5H), 1.59 (m, 0.5H), 1.50 (m, 0.5H), 0.97-1.02 (2d, 3H), 0.92 (s, 9H), 0.18 (s, 6H). **6f**: IR (CCl_4) 2956, 1711, 1686, 1492, 1463, 1364, 1309, 1254 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.30 (m, 5H), 6.49 (d, *J*=11.5 Hz, 1H), 5.72 (t, *J*=~11 Hz, 1H), 5.81 (dd, *J*=11.0, 15.4 Hz, 1H), 5.42 (d, *J*=15.4 Hz, 1H), 4.46 (s, 2H), 3.46 (t, 2H), 1.66 (t, 3H), 1.00 (s, 6H), 0.90 (s, 9H), 0.16 (s, 6H).

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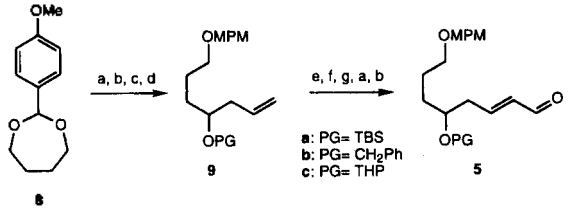
6. The very small amount of a diene, along with the (1*E*,

3*E*)-diene, was also present and the diene assumed as (1*E*,3Z)-diene on the basis of the stereochemical outcomes from **5d-f**.

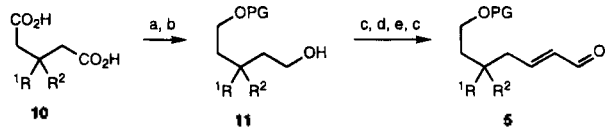
7. δ-Alkoxy-α,β-aldehydes **5a-c** were prepared as follows:



Reagents: (a) DIBAH, CH_2Cl_2, 0°C (b) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, -78°C (c) CH_2=$CHCH_2MgBr$, THF, 0°C (d)TBSCl, Et_3N, DMAP, CH_2Cl_2 for **9a**; NaH, $PhCH_2Br$, Bu_4NI, THF, reflux for **9b**; DHP, TsOH, CH_2Cl_2 for **9c** (e) OsO_4, NMO, acetone-H_2O (f) $NaIO_4$, THF-H_2O (g) NaH, $(MeO)_2P(=O)CH_2CO_2Me$, THF

8. The coupling constants of ~6 Hz are observed for (Z)-siloxy olefins. See: House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.

9. Enals **5d-f** were prepared as follows:



Reagents: (a) $LiAlH_4$, THF, reflux for **d**, **e** (b) TBDPSCl, Et_3N, CH_2Cl_2 for **5d**; NaH, $PhCH_2Br$, Bu_4NI, THF, reflux for **5e,f** (c) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, -78°C (d) NaH, $(MeO)_2P(=O)CH_2CO_2Me$, THF (e) DIBAH, CH_2Cl_2, 0°C

Structure of 1,3,5-Tris(*p*-fluorophenyl)hexahydro-1,3,5-triazine[1]

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1,3,5-Trisubstituted hexahydro-1,3,5-triazine as a source of N-methyleneamine equivalents in the presence of a Lewis acid were studied extensively in our laboratory.[2,3] Though the synthesis and utilities of 1,3,5-trisubstituted hexahydro-1,3,5-triazines were known for a long time little was revealed about their conformations.

The ample precedents can propose four possible conformers of **A-D** in the Figure 1 with different arrangements of three substituents on the chair form as the most stable conformer of the hexahydro-1,3,5-triazine. Crystal structure of 1,3,5-trinitro[4] and 1,3,5-triacetylhexahydro-1,3,5-triazines[5] showed the similar molecular structural features of the ring as a free cyclohexane geometry of chair from. Three nitro groups and three acetyl groups are inclined to the plane through the carbon ring atoms by approximately the angle of 18-62 °C and the similar angle of 48° respectively, *i.e.*

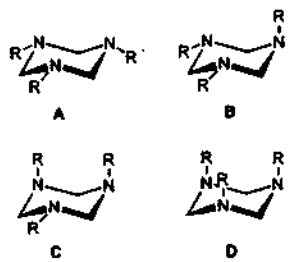

Figure 1. Four possible chair conformers of 1,3,5-trisubstituted hexahydro-1,3-5-triazine.

conformer **A**. 1,3,5-Trimethylhexahydro-1,3,5-triazines showed that three methyl groups are bonded equatorially to the hexahydro-1,3,5-triazine ring as a conformer **A**.[6] However, hexahydro-1,3,5-triazine bearing three neopentyl group has the similar ring structure of the chair form with one axial and two equatorial substituents in a crystal structure of the conformer **B**.[7]

With these attributes in mind we decide to study the conformation of the compound 1,3,5-tris(*p*-fluorophenyl)hexahydro-1,3,5-triazine, herein called TFPHT, synthesized from *p*-fluoroaniline and formaldehyde.[3a] This crystalline TFPHT is subjective for structural studies to answer the following questions, *i.e.* 1) What kind conformation the hexahydro-1,3,5-triazine ring has in the crystalline state and in solution, 2) How the three phenyl rings were attached to the ring. We report herein the conformational studies of TFPHT based on the X-ray structure and the calculated stable conformers with the programs of PM3[8] and MMX.[9]

The ring configurations of the title compound TFPHT in the solid state is similar to free cyclohexane structure of undistorted chair conformation that was observed in the all reported crystalline products as shown in Figure 2. Especially TFPHT has a symmetry plane bisected through N5 and C6. Geometric configurations of substituents on TFPHT are different from the others that all three or at least two substituents are bonded equatorially to the carbon atom of ring shown in conformer **A** and **B**. Among three *p*-fluorophenyl substituents on the ring two of them are bonded axially and the other one is bonded equatorially like the conformer **C**.