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HIGHLY DIASTEREOSELECTIVE SYNTHESIS OF (E)-1-TRIMETHYLSILYL-1-EN-3-YNES, (1E,3Z)- and (1E,3E)-1-TRIMETHYLSILYL-1,3-DIENES

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SUMMARY: In the stereospecific palladium-catalysed cross-coupling reaction of 1-alkynylzinc chlorides or (E)-1-alkenyl diisobutylalanes, (E)-2-bromovinyltrimethylsilane reacts preferentially, in the presence of the corresponding (Z)-stereoisomer to afford good yields of (E)-1-trimethylsilyl-1-en-3-ynes (4) or (1E,3E)-1-trimethylsilyl-1,3-dienes (6), respectively, having very high stereoisomeric purities. Compounds 4 are easily converted into (1E,3Z)-1-trimethylsilyl-1,3-dienes (5) by selective hydrometallation reactions, followed by protonolysis.

The overwhelming number of reports on the synthesis and use of organosilanes containing 1-alkynyl[1] or stereodefined 1-alkenyl[1], 1-en-3-ynyl[2,3], 3-en-1-ynyl[4], or 1,3-dienyl groups[5-7] linked to silicon shows that these reagents are excellent synthetic tools.

During our previous studies on highly diastereoselective palladium-catalysed cross-coupling reactions between 1-alkynylzinc chlorides and stereoisomeric mixtures of 1,2-dibromoethylene[2m] or 1-alkenyl bromides[2e], we have developed efficient procedures for synthesising (E)-1,6-bis(trimethylsilyl)-hexa-3-en-1,5-diyne (1)[2g] and (E)-1-trimethylsilyl-3-en-1-ynes (2)[2e]. Noteworthy, compounds 2 can be easily converted into (1Z,3E)-1-trimethylsilyl-1,3-dienes (3) by hydroalumination followed by hydrolysis with ice-cold 3 N NaOH[2d,2i].


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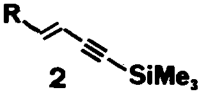
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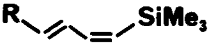
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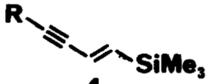
In continuation of these studies we now wish to report simple and convenient highly diastereoselective procedures for the synthesis of (E)-1-trimethylsilyl-1-en-3-ynes (4), (1E,3Z)-1-trimethylsilyl-1,3-dienes (5), and (1E,3E)-1-trimethylsilyl-1,3-dienes (6) starting from a commercially available stereoisomeric mixture of 2-bromovinyltrimethylsilane (7) which contains 87-92 % of the (E)-stereoisomer.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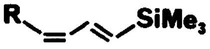
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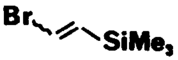
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Thus, when treated with 0.95 n equiv of an 1-alkynylzinc chloride (8) and 3 mole % of (PPh$_3$)$_4$Pd in THF at -20°- 0° for 2-4 h, a stereoisomeric mixture of 7 which contained n equiv of (E)-7 afforded good isolated yields of (E)-1-trimethylsilyl-1-alken-3-yne (4) having stereoisomeric purity higher than 99.5%. Some typical results are summarized in Table 1.

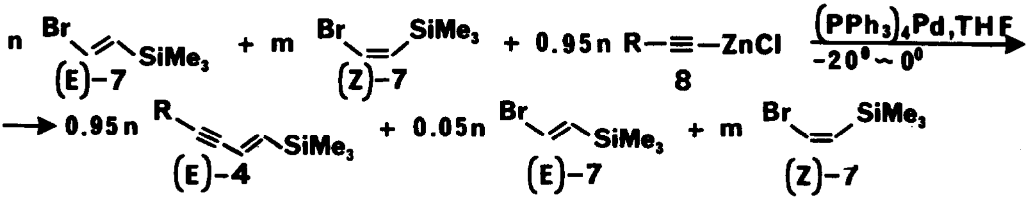


Table 1

Diastereoselective synthesis of (E)-1-trimethylsilyl-1-alken-3-ynes (4)

Reagent: 8		Reaction conditions		Product: (E)-4		
Compound	R	Temp. (°C)	Time (h)	Compound	Isolated yield (%)	Stereoisomeric purity (%)
8a	C_5H_{11}	0	2	4a	78	99.5
8b	Ph	- 15	4	4b[4a]	88	99.5
8c	$SiMe_3$	- 20	2	4c[4b,4c]	77	99.5

Owing to the high yields and the simplicity, this procedure is more convenient than those previously employed to prepare (E)-1-trimethylsilyl-1-en-3-ynes such as 4b[4a] and 4c[4b,4c].

In an attempt to develop a selective method for reducing the acetylenic group of compounds 4, some procedures previously employed to prepare (Z)-1-alkenylsilanes via hydromagnesiation[9], hydroalumination[10], or hydroboration[11] of the corresponding 1-alkynylsilanes were tested. It can be seen from Table 2 that different methods had to be employed to convert selectively and in satisfactory yield alkyl or silyl and aryl substituted (E)-1-trimethylsilyl-1-en-3-ynes (4) into the corresponding (1E,3Z)-dienes (5). Thus, compound 5a having 99.3 % stereoisomeric purity was obtained in 71 % yield by application of a hydroboration-protonolysis sequence (Entry 3). On the other hand, hydroalumination in ether, followed by hydrolysis of the derived dienylalane with ice-cold 3 N NaOH was used to prepare in 87 % yield compound 5b[2d] having 99.4 % stereoisomeric purity (Entry 4). This same method appears suitable to prepare compound 5c[5h] having high stereoisomeric purity, in spite of the modest conversion (Entry 6).

Finally, highly diastereoselective alkenylation reactions of (E)/(Z)-7 with (E)-1-alkenylalanes (9) were employed to prepare in high yield alkyl substituted (1E,3E)-1-trimethylsilyl-1,3-dienes (6)[12] having stereoisomeric purity higher than 99 %.

Table 2

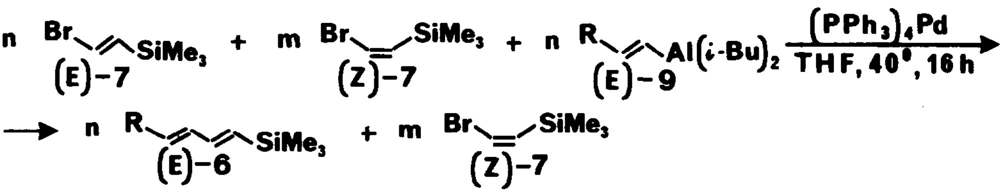
(1E,3Z)-1-Trimethylsilyl-1,3-dienes (5) from (E)-1-trimethylsilyl-1-en-3-ynes (4)

Entry	Product: 5		Procedure	Yield (%)	E / Z ratio [a]
	Compound	R			
1	5a[8]	C_5H_{11}	i) i-Bu$_2$AlH, hexane, 3.5 h at 25°, 3 h at 45°; ii) 3 N NaOH, 0°.	38[b,c]	94.2 / 5.8[f]
2	5a[8]	C_5H_{11}	i) i-BuMgBr, Cp$_2$TiCl$_2$, ether, 20 h; ii) H_2O, 0°.	14[b]	42.5 / 57.5[f]
3	5a	C_5H_{11}	i) Sia$_2$BH, THF, 3 h, 20°; ii) AcOH, 6 h, 70°; iii) H_2O_2, HO$^-$, 3.5 h, 25°.	71[d]	95.2 / 4.8[f] (99.3 / 0.7)[g]
4	5b[2d]	SiMe$_3$	i) i-Bu$_2$AlH, ether, 5.5 h, 35°; ii) 3 N NaOH, 0°.	87[d]	99.4 / 0.6 [f] (99.4 / 0.6)[g]
5	5c[5h]	Ph	i) i-Bu$_2$AlH, hexane, 24 h, 50°; ii) 3 N NaOH, 0°	19[d,e]	84.3 / 16.7[f]
6	5c[5h]	Ph	i) i-Bu$_2$AlH, ether, 32 h, 35°; ii) 3 N NaOH, 0°.	38[b,c]	96.2 / 3.8[f]
7	5c[5h]	Ph	i) Sia$_2$BH, THF, 5h, 0°; ii) AcOH, 7 h, 70°; iii) H_2O_2, HO$^-$, 3.5 h, 25°.	59[d]	(91.9 / 8.1)[g]

a) Evaluated by Glc/MS and ^1H NMR analyses; b) Evaluated by Glc analysis of the crude reaction mixture; c) The reaction mixture contained only the desired (1E,3Z)-silylated butadiene 5 and unreacted 4; d) Isolated yield; e) This compound was contaminated by ca.20 % of the corresponding (E)-monounsaturated silyl alkenes; f) E / Z ratio for the crude reaction mixture; g) E / Z ratio for the isolated product.

Typically, when a THF solution of a stereoisomeric mixture of 7 which contained n equiv of (E)-7 was allowed to react for 16 h at 40° with a hexane solution of (E)-1-heptenyl diisobutylalane (9a), in the presence of 3 mole % of $(PPh_3)_4Pd$, (1E,3E)-1-trimethylsilyl-1,3-nonadiene (6a)[5i] was obtained in 74.7 % isolated yield.

Analogously, (1E,3E)-1-trimethylsilyl-5,5-dimethyl-1,3-hexadiene (6b)[5a] was prepared in 84 % isolated yield starting from (E)-3,3-dimethyl-1-butenyl diisobutylalane (9b).



Applications of the above reported diastereoselective procedures to the synthesis of naturally-occurring polyunsatured compounds are in progress.

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6) For syntheses of (1Z,3E)-1-trimethylsilyl-1,3-dienes, see: a) Ref 2d; b) Ref 2g; c) Ref 5f.

7) For syntheses of (1E,3Z)-1-trimethylsilyl-1,3-dienes, see: a) Ref 5f; b) Ref 5h; c) Ref. 5p; d) Ref 4c.

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