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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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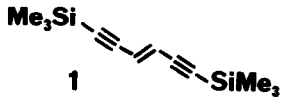
*SUMMARY: In the stereospecific palladium-catalysed cross-coupling reaction of 1-alkynylzinc chlorides or (E)-1-alkenyl diisobutylalanes, (E)-2-bromovinyltrimethylsilane reacts preferentially, in the presence of the corresponding (Z)-stereoisomer to afford good yields of (E)-1-trimethylsilyl-1-en-3-ynes (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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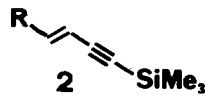

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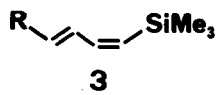

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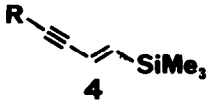
In continuation of these studies we now wish to report simple and convenient highly diastereoselective procedures for the synthesis of (E)-1-trimethylsilyl-1-en-3-ynes (4), (1E,3Z)-1-trimethylsilyl-1,3-dienes (5), and (1E,3E)-1-trimethylsilyl-1,3-dienes (6) starting from a commercially available stereoisomeric mixture of 2-bromovinyltrimethylsilane (7) which contains 87-92 % of the (E)-stereoisomer.



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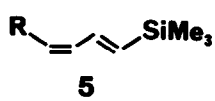

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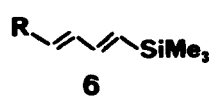

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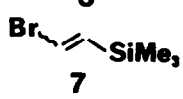

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Thus, when treated with 0.95 n equiv of an 1-alkynylzinc chloride (8) and 3 mole % of $(PPh_3)_4Pd$ in THF at -20°- 0° for 2-4 h, a stereoisomeric mixture of 7 which contained n equiv of (E)-7 afforded good isolated yields of (E)-1-trimethylsilyl-1-alken-3-yne (4) having stereoisomeric purity higher than 99.5%. Some typical results are summarized in Table 1.

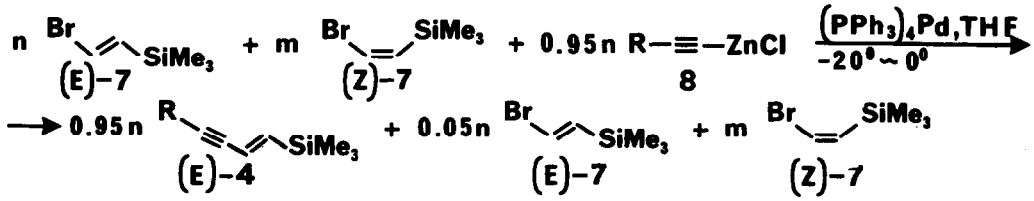



Table 1

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

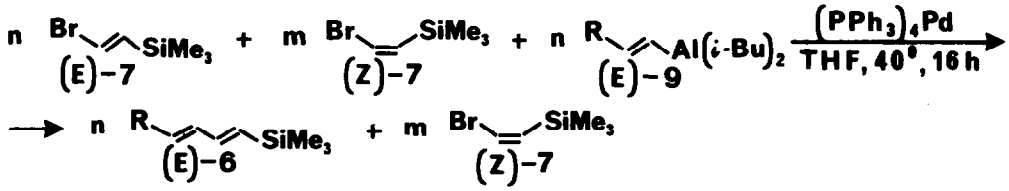
(1E,3Z)-1-Trimethylsilyl-1,3-dienes (5) from (E)-1-trimethylsilyl-1-en-3-ynes (4)

| Entry | Product: 5 | | Procedure | Yield (%) | E / Z ratio [a] |
|---|---|---|---|---|---|
| | Compound | R | | | |
| 1 | 5a[8] | $C_5H_{11}$ | i) *i*-$Bu_2AlH$, 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, $Cp_2TiCl_2$, ether, 20 h; ii) $H_2O$, 0°. | 14[b] | 42.5 / 57.5[f] |
| 3 | 5a | $C_5H_{11}$ | i) $Sia_2BH$, 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*-$Bu_2AlH$, 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*-$Bu_2AlH$, hexane, 24 h, 50°; ii) 3 N NaOH, 0° | 19[d,e] | 84.3 / 16.7[f] |
| 6 | 5c[5h] | Ph | i) *i*-$Bu_2AlH$, ether, 32 h, 35°; ii) 3 N NaOH, 0°. | 38[b,c] | 96.2 / 3.8[f] |
| 7 | 5c[5h] | Ph | i) $Sia_2BH$, 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.

8) All new compounds exhibited satisfactory spectral and physical properties.

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12) Owing to the difficulty in preparing chemically pure (E)-1-alkenylalanes by hydro-alumination of (hetero)arylacetylenes (J. J. Eisch, M. W. Foxton, J. Org. Chem., 36, 3520 (1971); R. Köster, P. Binger, Adv. Inorg. Chem. Radiochem., 7, 317 (1965) ), no attempt was performed to use these palladium-catalysed alkenylation reactions for synthesising (hetero)aryl substituted (1E,3E)-1-trimethylsilyl-1,3-dienes.

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