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# STEREOSPECIFIC SYNTHESES OF *CIS*- AND *TRANS*-1,6-BISTRIMETHYLSILYL-HEX-3-ENE-1,5-DIYNE

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**Abstract:** Stereospecific syntheses of the title compounds were achieved via the palladium-catalyzed bisethynylation of the vicinal dichloroethenes.

The palladium-catalyzed synthesis of substituted alkenes from vinyl halides has recently received considerable attention.[1] During the course of a project aimed at the preparation of stereospecifically deuterated 1,3,5-hexatrienes we considered the use of the title compounds as intermediates and their preparation by this strategy. While **1a** and **2a** are unknown, the quite sensitive parent *cis*- and *trans*-hex-3-ene-1,5-diynes have been synthesized by relatively lengthy and nonstereospecific routes.[2] We report here the facile stereospecific, catalytic double coupling of trimethylsilylethyne (tmse) with *cis*- and *trans*-1,2-dichloroethene, to our knowledge an unprecedented reaction of vicinal dichloroalkenes.[3] We are prompted to disclose our results by a related preparation of **1a** and **2a** via a less straightforward nickel-catalyzed Grignard reaction.[4]

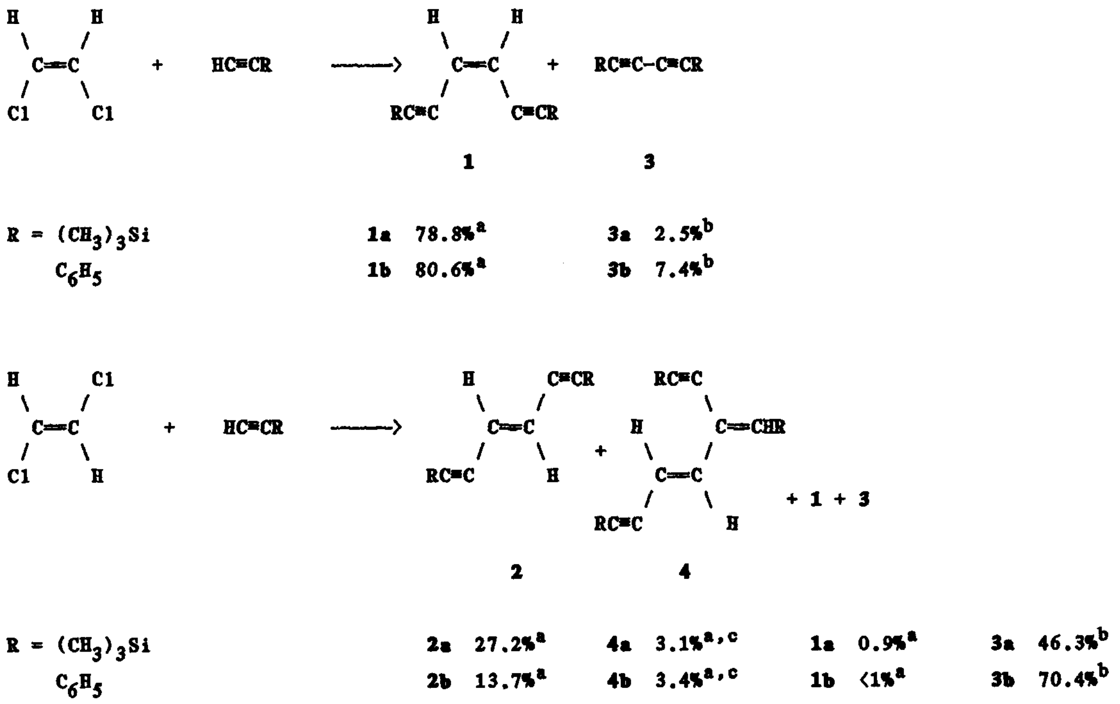
The synthesis of **1a** exemplifies the general method followed (Scheme I). A solution of tmse (2.77g, 28.3 mmole) in benzene was added via syringe to a solution of *cis*-1,2-dichloroethene (99.3% *cis*, 1.29g, 13.3 mmole), *n*-butylamine (2.98g, 40.8 mmole), tetrakis(triphenylphosphine)-palladium (0) (0.9g, 0.77 mmole), copper(I) iodide (0.19g, 1.8 mmole), and benzene under argon. The reaction mixture was allowed to stir at ambient temperature for 1 h. The crude product (3.4g) contained 85.1% **1a** and 2.0% of the coupled alkyne **3a**. The *trans*-isomer **2a** was not detected by GC or NMR. Further purification by vacuum transfer afforded **1a** as a colorless oil (2.30g, 78.8%).[5] Assignment of the stereochemistry of **1a** (and later **2a**) was based on the respective *cis* (J=10.9 Hz) [and *trans* (J=16.3 Hz)] coupling constants obtained from the $^{13}C$ satellite proton NMR spectra.

Similarly, high yielding stereospecific coupling with *cis*-1,2-dichloroethene was observed when the terminal alkyne was phenylethyne (*cis*-**1b**; 80.6%, no *trans*-**2b** could be detected).[5]

In the absence of copper (I) iodide, no reaction occurred. Using tetrakis(triphenylphosphine)-platinum(0) or bis(triphenylphosphine)nickel (II) dichloride as catalysts, none of the desired products were isolated.

The synthesis of **2a** proceeded more slowly and in reduced yields. After 14 h at ambient temperatures, **2a**[5] was isolated in 27.2% yield from the coupling reaction of *trans*-dichlorethene (97.7% *trans* and 2.3% *cis*) and tmse. The *cis*-product **1a** formed in this preparation (0.9%) undoubtedly resulted from the *cis*-1,2-dichloroethene impurity present in the starting alkene. The alkyne **3a** and a second side product **4a** were also isolated from this reaction. The latter had spectral data consistent with the structure given in Scheme I[5] and probably resulted via hydroethynylation of **2a**. At elevated temperatures (35–45°C) the yield of **3a** decreased, but the yield of **4a** increased. Increasing the catalyst concentration or reducing the rate of alkyne addition did not affect the yield of the desired product.

**Scheme I**



| R = | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $(CH_3)_3Si$ | **1a** | 78.8%[a] | **3a** | 2.5%[b] | | | | |
| $C_6H_5$ | **1b** | 80.6%[a] | **3b** | 7.4%[b] | | | | |

| R = | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $(CH_3)_3Si$ | **2a** 27.2%[a] | | **4a** 3.1%[a,c] | | **1a** 0.9%[a] | | **3a** 46.3%[b] | |
| $C_6H_5$ | **2b** 13.7%[a] | | **4b** 3.4%[a,c] | | **1b** <1%[a] | | **3b** 70.4%[b] | |

[a] Yields based on starting dichloroethene for the products isolated after chromatography.
[b] Yields based on starting alkyne for the products isolated after chromatography.
[c] Structural assignment based on $^{13}C$ NMR, $^{1}H$ NMR and HRMS.

The use of phenylethyne in the coupling with *trans*-1,2-dichloroethene gave a similar product mixture; the *trans*-product **2b**[6] was obtained in 13.7% yield with less than 1% of the *cis*- product **1b**.

The coupling reaction of *cis*-1,2-dichloroethene required shorter reaction times than the coupling of the *trans*-isomer. We also found that the coupling of tmse and a mixture of *cis*- and *trans*-1,2-dibromoethenes (12.8 mmol; 69.6% *trans* and 30.4% *cis*) afforded a low yield (0.34g) product mixture. The major component of which was the *cis*-compound **1a** (86.4%) with minor amounts of **2a** (1.6%) and **3a** (11.5%) also present.

The greater reactivity of the *cis*-1,2-dichloroalkenes can be accounted for by assuming that the reaction involves stepwise oxidative addition of the halide bonds to palladium. It is presumed that the palladium does not dissociate from the molecule, but is trapped by the adjacent vinyl halide moiety. Conversely, in the *trans*-series, the metal might have to dissociate prior to the second oxidative addition. Competing hydropalladation of the alkyne would then be possible.

The reported method suggests an efficient route to enediynes from readily available 1,2-dichloroethenes and terminal alkynes. Partial reduction of these compounds should result in the synthesis of terminally substituted trienes. Investigations toward this goal are currently in progress.

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## References and Notes

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2. Bergman, R.G. *Acc. Chem. Res.* **1973**, *6*, 25. Figeys, H.P.; Gelbcke, M. *Tetrahedron Lett.* **1970**, *59*, 5139. Jones, R.R.; Bergman R.G. *J. Am. Chem. Soc.* **1972**, *94*, 660. Okamura, W.H.; Sondheimer, F. *Ibid.* **1967**, *89*, 5991.
3. For the transition metal mediated single coupling reactions of chloroalkenes see: Ratovelomanana, V.; Linstrumelle, G. *Synth. Comm.* **1984**, *14*, 179 and the references therein.
4. Walker, J.A.; Bitler, S.P.; Wudl, F. *J. Org. Chem.*, in press. We thank Professor Wudl for communicating his results prior to publication.
5. **1a**: Colorless oil; IR (thin film) 3043, 2961, 2900, 2158, 2124, 1680, 1568, 1448, 1410, 1388, 1252, 1206, 1072, 1005, 980, 847, 762, 702, 636 $cm^{-1}$; $^{1}H$ NMR (300 MHz, $C_6D_6$) δ 5.50 (s, 1 H), 0.19 (s, 9 H); $^{13}C$ NMR (300 MHz, $C_6D_6$) δ 122.2 ($J_{13C-H}$=168.8 Hz) 105.5, 101.2, -0.23; MS (rel intensity) *m/e* 220 (28), 73 (100). Anal. Calcd for $C_{12}H_{20}Si_2$: C, 65.38; H, 9.14. Found: C, 65.12; H. 9.09.

   **1b**: White needles, mp 33-34°C (from MeOH); IR (thin film) 3080, 3060, 2220, 2180, 1675, 1600, 1570, 1490, 1445, 1405, 1070, 1030, 915, 755, 690 $cm^{-1}$; $^{1}H$ NMR (300 MHz, $CDCl_3$) δ 7.55 (m, 2 H), 7.36 (m, 3 H), 6.12 (s, 1 H, $J_{HH}$=10.6 Hz); $^{13}C$ NMR (300 MHz, $CDCl_3$) δ 131.7, 128.8, 128.4, 123.1, 119.4 ($J_{13CH}$= 169.5 Hz), 97.6, 87.3; MS (rel intensity) *m/e* 228 (100). **2a**: Light yellow plates, mp 75-76°C (from EtOH-$H_2O$); IR ($CHCl_3$) 3000, 2950, 2390, 2160, 2120, 2060, 1245, 1200, 1090, 845 $cm^{-1}$; $^1H$ NMR (300 MHz, $C_6D_6$) δ 6.11 (s, 1 H), 0.10 (s, 9 H); $^{13}C$ NMR (300 MHz, $C_6D_6$) δ 120.9 ($J_{13CH}$=167.8 Hz) 103.4, 102.9, -0.07; MS (rel intensity) *m/e* 220 (27), 205 (100); HRMS calcd for $C_{12}H_{20}Si_2$: 220.1104; found: 220.1105. **2b**: Light yellow needles, mp 107-109°C, (from MeOH/$H_2O$); $^1H$ NMR (300MHz, $CDCl_3$) δ 7.45 (m, 3 H), 7.34 (m, 2 H), 6.33 (s, 1 H); $^{13}C$ NMR (300 MHz, $CDCl_3$) δ 131.6, 128.6, 128.3, 122.8, 120.6, 94.9, 88.1; MS *m/e* 228 (100);

**4a**: $^1H$ NMR (300 MHz, $CDCl_3$) δ 6.64 (d, J=15.6 Hz, 1 H), 6.23 (s, 1 H), 6.08 (d, J=15.4 Hz, 1 H), 0.20 (s, 9 H), 0.19 (s, 9 H), 0. 17 (s, 9 H); $^{13}C$ NMR (300 MHz, $CDCl_3$) δ 144.9, δ 139.7, 134.4, 115.7, 103.9, 103.0, 100.0, 96.0, 0.004, -0.09 (2C); HRMS calcd for $C_{17}H_{30}Si_3$: 318.1655; found: 318.1657.

**4b**: $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.45 (m, 15 H), 6.30 (broad s, 1 H), 6.24 (broad s, 1 H), 6.09 (broad s, 1 H); $^{13}C$ NMR (300 MHz, $CDCl_3$) δ 132.5, 131.7 (2C), 131.6 (2C), 128.7, 128.6 (2C), 128.3 (2C), 128.1, 122.8, 122.7, 121.4, 120.2, 119.4, 95.7, 94.8, 93.6, 88.1, 88.0; MS (rel intensity) *m/e* 330 (3), 276 (100); HRMS calcd for $C_{26}H_{18}$: 330.1408; found: 330.1403.

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