# Synthesis of 1-Trimethylsilylcycloalkenes from 1-Bromocycloalkenes by Wurtz-type Coupling

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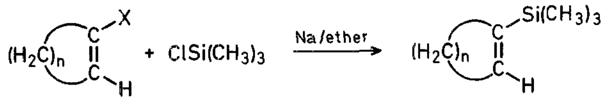
Vinylsilanes are acquiring increasing importance in recent years as intermediates in synthetic organic chemistry[1]. For the synthesis of acyclic vinylsilanes several general methods are available[1a], which are not normally applicable for cyclic vinylsilanes. There are some examples of obtaining cyclic vinylsilanes from the corresponding vinyl halides through metallation followed by silylation[2]. A method to prepare small amounts of cyclic vinylsilanes starting from cycloalkanones has also been developed[3]. However, these methods are not quite suitable for large scale syntheses.

1-Trimethylsilylcyclohexene, which has found use as a starting compound in the elucidation of reaction mechanisms of $\alpha,\beta$-epoxysilanes[4], was first synthesised by Petrov et al. by the Wurtz-type coupling of 1-chlorocyclohexene with chlorotrimethylsilane[5]. Surprisingly, there is no report of exploitation of this simple reaction for the preparation of any other vinylsilane.

Because of our interest in medium ring compounds[6], we needed medium and large ring vinylsilanes in a study to compare the reactions of their epoxides with acyclic and normal ring $\alpha,\beta$-epoxysilanes[7]. In extending the Wurtz-type reaction to other ring systems, we found that cyclic vinyl bromides in general are much superior to their chloro-analogues as starting haloolefins. They not only give better yields but are more reactive, and hence require comparatively shorter reaction times. Moreover, in the case of medium and large rings, it is much easier to obtain their vinyl bromides in pure form and good yields starting from easily available cycloalkenes than the corresponding vinyl chlorides, which are usually prepared by the reaction of cycloalkanones with phosphorus pentachloride[8]. 1-Bromocycloalkenes can also be obtained by ring expansion reactions of *gem*-dibromocyclopropane derivatives[9].

We have used 1-bromocycloalkenes (**2a-e**) as well as their chloro-analogues (**1a-e**) for the present study, and the results are summarised in the Table.



**1a-e** X = Cl
**2a-e** X = Br

**3a-e**

The tabulated results show that cyclic vinyl bromides are better starting compounds for the Wurtz-type reaction to prepare vinylsilanes; their use gives better yields, requires

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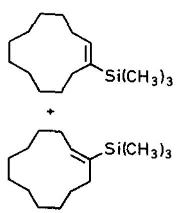
**Table.** 1-Cycloalkenyltrimethylsilanes **3a–e**

| Product | | Starting material[a] | Reaction conditions | Yield [%][b] | Purity [%][c] | b.p. [°C]/torr found | b.p. [°C]/torr reported | I.R. (neat) $\nu$ [cm$^{-1}$] | $^1$H-N.M.R. CDCl$_3$/60 MHz) $\delta$ [ppm] | M.S. *m/e* (rel. intensity %) |
|---|---|---|---|---|---|---|---|---|---|---|
| **3a** | n=3 | **1a**[11]<br>**2a**[12] | reflux (60 °C)/4–5 h<br>r.t./6–8 h | 50<br>59 | 90<br>93 | 55–57°/50 | 160–170°[2]; 144°[17] | 3030, 2950, 2890, 2840, 1595, 1250, 840, 690 | 0.07 (s, 9H); 1.6–2.1 (m, 2H); 2.1–2.7 (m, 4H); 6.1 (m, 1H) | 140 (17, M$^+$); 125 (95); 97 (97); 73 (100); 59 (34); 45 (18); 43 (26) |
| **3b** | n=4 | **1b**[13]<br>**2b**[14] | r.t./7–8 h<br>r.t./3–4 h | 78<br>83 | 98<br>98 | 75–77°/16 | 171.5°/752[5] | 3010, 2940 2920, 2840, 1620, 1450, 1250, 1140, 1065, 940, 835, 745, 685 | 0.06 (s, 9H); 1.5–1.9 (m, 4H); 1.9–2.3 (m, 4H); 6.1 (m, 1H) | 154 (8, M$^+$); 139 (20); 111 (14); 80 (24); 74 (10); 73 (100); 59 (30); 45 (12) |
| **3c** | n=5 | **1c**[8]<br>**2c**[12] | r.t./7–8 h<br>r.t./4–5 h | 58<br>77 | 85<br>96 | 65–67°/10 | —[3] | 3020, 2960, 2930, 2860, 1620, 1450, 1245, 925, 850, 835, 745, 685 | 0.06 (s, 9H); 1.2–2.0 (m, 6H); 2.0–2.4 (m, 4H); 6.27 (t, $J$=6 Hz, 1H) | 168 (4, M$^+$); 153 (15); 125 (12); 94 (26); 93 (10); 74 (9); 73 (100); 59 (37); 45 (11) |
| **3d** | n=6 | **1d**[8]<br>**2d**[15] | r.t./5–6 h<br>r.t./3–4 h | 71<br>89 | 78<br>99 | 91–92°/8 | 73–74°/7[10] | 2990, 2940, 2920, 2840, 1615, 1470, 1450, 1250, 1000, 905, 890, 835, 750, 680 | 0.04 (s, 9H); 1.3–1.8 (m, 8H); 1.8–2.5 (m, 4H); 6.10 (t, $J$=8 Hz, 1H) | 182 (1.5, M$^+$); 167 (10); 139 (12); 108 (31); 80 (7); 79 (10); 74 (9); 73 (100); 59 (31); 45 (10) |
| **3e**[d] |  | **1e**[8] (Z:E=62:38)<br>**2e**[16] (Z:E=58:42) | reflux (60 °C)/4 d<br>reflux (60 °C)/8–10 h | 60<br>73 | 84<br>93 | 125–128°/1 | — | 2940, 2865, 1610, 1585, 1470, 1450, 1250, 835, 750, 680 | 0.06 + 0.15 (2s, 9H); 1.1–1.8 (m, 16H); 1.8–2.5 (m, 4H); 5.80 + 6.22 (t, $J$=7.7 Hz + t, $J$=7.8 Hz, 1H) | *cis:* 238 (2.5, M$^+$); 223 (6); 164 (31); 135 (17); 121 (16); 99 (15); 82 (15); 81 (18); 74 (27); 73 (100); 67 (16); 59 (40); 45 (18)[e]<br>*trans:* 238 (2, M$^+$); 223 (4); 164 (27); 135 (16); 121 (17); 99 (18); 82 (23); 81 (23); 74 (33); 73 (100); 67 (22); 59 (55); 45 (27)[e] |

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[a] All haloolefins were prepared by known procedures.

[b] Yield of isolated products.

[c] G.L.C. analyses were performed using a Varian 1400 chromatograph; column: 3 m, 5% Carbowax 20M on Chromosorb P or 3.5 m, 2.5% nitrilsilicone oil on Chromosorb P; temperature program 60–160 °C at 4 or 8 °C/min.

[d] $C_{15}H_{30}Si$ (238.5) calc. C 75.54 H 12.68; found 75.47 12.50

[e] Combined GC-MS.

shorter reaction times, and milder conditions. This superiority is also illustrated in the case of 12-membered ring system. Another point to be noted is that this method works equally well for large and small scale preparations.

We noticed that the reaction of phosphorus pentachloride with medium ring ketones gives complex mixtures of products from which the desired chloroolefins were isolated in <85% purity. However, such a problem was not encountered with cyclopentanone and cyclohexanone. Cyclododecanone gave a 62:38 mixture of *trans*-1- and *cis*-1-chlorocyclododecene which yielded the corresponding vinylsilanes in the same ratio. From the 58:42 mixture of *trans*-1- and *cis*-1-bromocyclododecene also we obtained the *trans*- and *cis*-vinylsilanes in the same ratio. We conclude, therefore, that there is probably no isomerisation taking place during silylation.

**1-Trimethylsilylcyclooctene (3d):**
To sodium wire (33.3 g, 1.45 mol; granular sodium gives equally good results) in ether (350 ml) stirred under a nitrogen atmosphere is added chlorotrimethylsilane (66.8 g, 0.61 mol) in one portion. After stirring of the mixture for 15 min, 1-bromocyclooctene[15] (**2d**; 86.5 g, 0.458 mol) is added over a period of 1 h. During addition and 30–60 min thereafter, the reaction mixture becomes slightly warm and refluxes gently. By the time the refluxing subsides more than 90% of the starting bromide is found to have reacted. After stirring the reaction mixture for an additional 3 h, excess sodium and solid products are filtered off through a plug of glass wool and the residue is washed with ether (2 × 30 ml). The combined filtrates are carefully washed with saturated sodium hydrogen carbonate solution (100 ml), water (2 × 150 ml), and finally with saturated sodium chloride solution, then dried with magnesium sulphate, and concentrated. On distillation, product **3d** of 99% purity is obtained; yield: 74.1 g (89%); b.p. 91–92 °C/8 torr.

**1-Trimethylsilylcyclododecene (3e):**
To sodium wire (6.0 g, 260.9 mmol) in ether (75 ml) under nitrogen is added chlorotrimethylsilane (12.84 g, 118.2 mmol). After stirring the mixture for 15 min, 1-bromocyclododecene (**2e**; 58:42, *trans*:*cis* mixture; 17.5 g, 73.4 mmol) is added over 15 min. The reaction mixture is then heated to reflux in an oil bath at 60 °C for 8 h, cooled, and worked up as described above to give **3e** as a 58:42 *trans*:*cis* mixture; yield: 12.40 g (73%); b.p. 125–128 °C/1 torr.

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